INL/EXT-08-14017

Evaluation of Aqueous and Powder Processing Techniques for Production of Pu-238-Fueled General Purpose Heat Sources

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Idaho National Laboratory

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Stephen G. Johnson — JUNE 23, 2008

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EXECUTIVE SUMMARY

This report evaluates alternative processes that could be used to produce Pu-238 fueled General Purpose Heat Sources (GPHS) for radioisotope thermoelectric generators (RTG). Fabricating GPHSs with the current process has remained essentially unchanged since its development in the 1970s. Meanwhile, 30 years of technological advancements have been made in the fields of chemistry, manufacturing, ceramics, and control systems. At the Department of Energy's request, alternate manufacturing methods were compared to current methods to determine if alternative fabrication processes could reduce the hazards, especially the production of respirable fines, while producing an equivalent GPHS product. An expert committee performed the evaluation with input from four national laboratories experienced in Pu-238 handling. The objectives of the evaluation are:

Objective 1: Minimize the potential for airborne radioactive contamination release during fabrication.

Objective 2: Reduce personnel radiation exposure during fabrication.

Objective 3: Reduce cracking of the unclad pellets while satisfying impact tests and operating performance requirements.

The process alternatives assume an aqueous feed stream of purified Pu-238 nitrate solution and produce an unclad GPHS pellet that meets all material and performance specifications. Thus, the scope of the evaluation specifically did not consider (a) heat generation from isotopes other than Pu-238, (b) alternate heat source geometries, and (c) other fuel matrices.

For this evaluation, the process steps were grouped into two subprocesses—production of green granules and pellet production. The current process consists of 10 distinct processing steps. Current granule production includes: (1) oxalate precipitation/filtering/drying, (2) oxide conversion, (3) O-16 exchange, (4) comminution through ball milling, (5) cold pressing, (6) granulation, and pellet production includes: (7) granule seasoning, (8) charge blending and die loading, (9) hot pressing, and (10) sintering.

The committee utilized professional judgment and reviewed literature to identify alternative processes that could be used to produce granules or pellets. The committee met April 21-24, 2008, in Idaho Falls, Idaho, to evaluate and prioritize these processes. The evaluation was hindered by the lack of available information on some of the processes. Many of the processes have not been investigated with Pu-238, preventing selection of a single alternative. A weighted set of evaluation criteria was developed considering hazard minimization, process simplicity, process control, chemical purity, and technical risk. Based on the committee's expertise, the list of process alternatives was winnowed to a small number that warrant further testing as shown in the table below.

Granule Production Methods	Pellet Production Methods
Precipitation methods	**Hot pressing methods**
• Improved oxalate precipitation	• Improved hot pressing and sintering
• Hydroxide precipitation	• Spark plasma sintering
• Granat flocculation	• Superplastic forming
• Ammonium plutonyl carbonate precipitation	
Alternate granule methods	**Alternate pressing methods**
• Modified direct denitration	• Preforming and pressureless sintering
• Sol-gel microsphere	
• Resin bead loading and calcination	

The committee considered pairing the granule and the pellet production processes to define an optimum integrated process, but determined that most of the granulate processes would work with any of the pellet production processes. The committee developed the following findings and recommendations.

Finding 1 – The existing product specifications are essentially process specifications. Physical characteristics of the GPHS product are not specifically measured and controlled. Rather, the fabrication process and operating parameters are tightly controlled to ensure consistency between new batches and the original product, and thus tie to the flight-qualification database. The physical characteristics require additional research if the reference process is to be modified.

Finding 2 – Several processes potentially can achieve the objectives. The preferred granule and pellet process alternatives are (a) the improved oxalate precipitation granule production and (b) the improved hot pressing pellet production.

Finding 3 – Other alternative processes entail higher risk but offer potentially higher rewards. Further reduction in dust generation, simpler operations and improved stress distributions may be achieved.

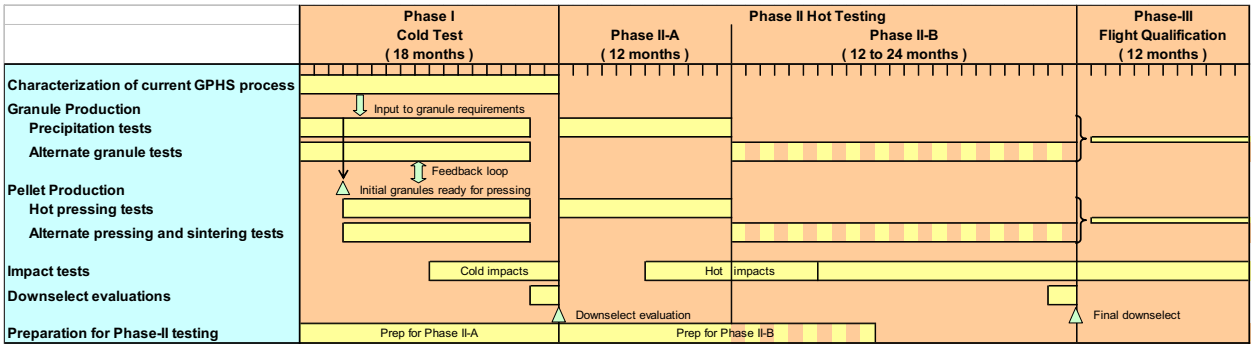
Recommendation 1 – Characterization should be performed on the current LANL Pu-238 process to document the physical characteristics of GPHS in-process material and final products as soon as possible.

Recommendation 2 – Final selection of a new Pu-238 process should be based on (1) test results from cold surrogate, Pu-239 surrogate, and Pu-238 testing, (2) optimized process parameters that produce the most repeatable product with the highest quality and (3) ability to produce GPHS pellets that can be readily qualified for space flight. The committee therefore recommends a staged test program, eliminating at each stage any processes that do not warrant further consideration.

Recommendation 3 – Investigate the processes identified in the table. Approximately $5 M over a two year period is needed for university/laboratory studies to complete initial cold surrogate testing. Funding would be used to conduct literature reviews, to perform testing, including impact testing, to answer key technical uncertainties; and to further downselect alternatives.

Recommendation 4 – Prepare for Pu-239 and follow-on Pu-238 testing of the preferred alternatives following down selection of process alternatives. These preparations will require a year or more and can be performed in parallel with surrogate testing.

The figure below depicts a timeline for selecting a final Pu-238 GPHS fabrication process and qualifying the new process for space flight.



This report is the consensus of the evaluation committee and the four concerned DOE laboratories: Idaho National Laboratory, Los Alamos National Laboratory, Oak Ridge National Laboratory and Savannah River National Laboratory.

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FIGURES

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ACRONYMS

ALE	Arbitrary Lagrangian-Eulerian (code)
ANSI	American National Standards Institute
APuC	ammonium plutonyl carbonate precipitation
AUPuC	ammonium uranyl plutonyl carbonate
CEDE	committed effective dose equivalent
DOE	Department of Energy
FIB	focused ion beam
FSA	fuel sphere assemblies
GPHS	General Purpose Heat Sources
ICRP	International Commission on Radiation Protection
INL	Idaho National Laboratory
LANL	Los Alamos National Laboratory
MDD	modified direct denitration
MOX	mixed (uranium and plutonium) oxide fuel
NASA	National Aeronautics and Space Administration
NCRP	National Council on Radiation Protection
NEPA	National Environmental Policy Act of 1969
ORNL	Oak Ridge National Laboratory
PPO	pure plutonium oxide
PUFF	Plutonium Fuel Fabrication Facility
RBAO	reaction bonded aluminum oxide
RBPO	reaction bonded plutonium oxide
RPS	radioisotope power system
RTG	radioisotope thermoelectric generator
SPH	smooth-particle hydrodynamics
SPS	spark plasma sintering
SRL	Savanna River Laboratory
SRS	Savannah River Site
SVT	safety verification test
TD	theoretical density
TZP	tetragonal polycrystalline zirconia
USAEC	United States Atomic Energy Commission

Evaluation of Aqueous and Powder Processing Techniques for Production of Pu-238 Fueled General Purpose Heat Sources

1. PURPOSE/OBJECTIVE

This report evaluates alternate processes that could be used to produce Pu-238 fueled General Purpose Heat Sources (GPHS) for radioisotope power systems (RPSs). The Department of Energy (DOE) is responsible for producing, processing, and packaging nuclear material for the RPS program and providing a launch safety data package for the National Aeronautics and Space Administration (NASA). It was developed during the 1960s and 1970s and has not significantly progressed since its inception. Meanwhile, decades of technological advancements have been made in the applicable fields of chemistry, manufacturing, ceramics, and control systems. This report considers alternate chemical and mechanical manufacturing methods, compares them to the current processing methods, and recommends a development strategy toward qualifying a new process. The objectives of the evaluation are:

Objective 1: Eliminate the potential for airborne radioactive contamination release during fabrication of GPHS pellets.

The current process requires milling Pu-238 material into a fine powder (less than 1 μm). Experience has shown that powder particulates less than 10 μm maximize risk for personnel exposure by inhalation and dispersion to the environment. In addition, this small particle size increases the mobility of the Pu-238 material by airflow and recoil energy produced during alpha decay. These factors increase contamination spread, make decontamination more difficult, and enhance the material's corrosive nature. Pu-238 interacts with process equipment, increasing breakdown and repair times. The fine powder is more difficult to confine, degrades and penetrates gloves and rubber seals, and increases the complexity of transferring material without spreading contamination.

To meet this objective, the researchers evaluated fabrication techniques that produce feed powder with particle sizes greater than 10 μm, thus eliminating the production of respirable fines during processing. Another complimentary approach is to use new, self-containing equipment, which is briefly discussed.

Objective 2: Reduce personnel radiation exposure during fabrication of GPHS pellets.

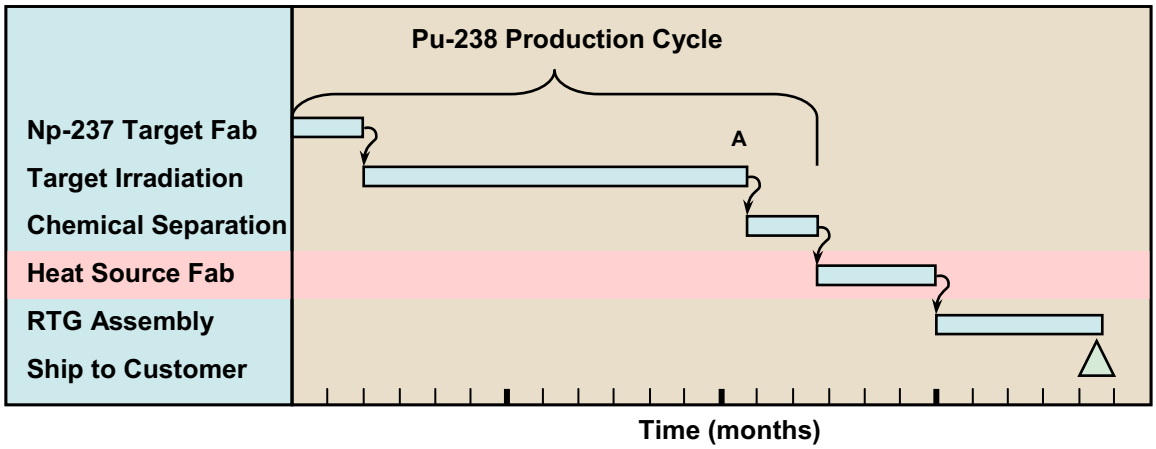
Radiation exposure to operating personnel is a major consideration in the current production of GPHS pellets. Exposure comes from several manual operations required during fabrication, and fine powder that spreads throughout the fabrication equipment and glovebox system. Three basic approaches are proposed to meet this objective: eliminate fines production, simplify the process by eliminating steps where possible, and eliminate manual operations.

Objective 3: Improve the structural integrity of the unclad pellets while satisfying impact test and operating performance requirements.

Using the current process, heat source pellets routinely contain cracks after fabrication. Occasionally the pellets break apart during handling before being installed into an iridium clad. Alternate fabrication methods may improve the integrity of the finished pellet while satisfying the necessary performance requirements. This will further decrease radiation dose associated with recycle and rehandling.

1.1 Scope

This evaluation considers the fabrication of GPHS pellets using Pu-238 oxide. Other activities required to manufacture radioisotope thermoelectric generators (RTGs) include fabricating Np-237 targets, producing Pu-238 in a reactor, and chemically separating Pu from irradiated targets as shown in Figure 1-1. Following their fabrication, GPHS pellets are clad, assembled into the RTG, tested, and delivered to the end-user for installing into the powered system. The process alternatives begin with assuming Pu-238 is purified and contained in an aqueous feed of nitrate solution. The alternatives conclude with an unclad GPHS pellet that meets all current material and performance specifications and will require minimal if any perturbation to the existing launch safety analysis.



A) Irradiation and cooldown cycle can vary between 9 months and 5 years depending on reactor neutron flux, fission product decay, and U-236 impurity.

Figure 1-1. RTG life cycle using Pu-238 fueled heat sources.

The decision to evaluate processes for making GPHS pellets is based on the current plans for RTG deployments. The GPHS was developed in the 1970s and all NASA missions in the past 30 years have used this design. Other current heat source designs that use the shard-type heat source can theoretically use the same granules produced by the GPHS process. Fuel for these alternate heat sources would exit the GPHS process after sintering the granules and before pressing the granules into pellets. Therefore, the alternate processes envelope most current heat source designs.

This evaluation does not consider (a) heat generation from isotopes other than Pu-238, (b) alternate heat source geometries, and (c) other fuel matrices. A discussion on alternate isotopes is provided in Appendix E. Considering the cost and time investment in developing the GPHS design, alternate heat source designs are beyond the scope of this report. Neither DOE nor the NASA has expressed an interest in moving to a different heat source design. Alternate fuel forms, other than iridium-clad, plutonium-oxide pellets are postulated in Section 5.4, Alternate Fuel Forms. While international research is continuing in this field, the remaining development effort to implement an alternate fuel form is judged to be too great for inclusion in this evaluation.

Alternative selection is limited by available information and limited testing of alternatives with Pu-238 oxide. While a committee of nationally recognized experts was assembled to evaluate process improvements, the behavior of Pu-238 in the various processes can only be postulated based on extrapolation from industry data with other materials and, when available, limited testing of Pu-238. This limitation prohibits selecting one definitive process. Therefore, the evaluation reduces the list of process alternatives to a small number that warrant further testing. Final selection should be based on (1) test results, (2) development of process parameters that produce the most repeatable product with the highest quality, and (3) the pellet with attributes that have the greatest potential of qualifying for space flight.

2. BACKGROUND

Since its beginning in the late 1950s, the RTG program has undergone many changes. The isotope selection, fuel form, facilities and production process have all advanced. The isotope selection will be discussed further in Section E-1. Other topics are discussed briefly below for general knowledge.

2.1 Fuel Forms

The fuel form has evolved during the first 20 years of RPS development. The primary driver for improving the fuel form has been improved safety under all accident conditions, including launch failures and orbital reentry. Reducing the power system size and weight has been another important motivation.

Initial heat sources SNAP-3B and SNAP-9A used metallic plutonium and were designed to burn up on reentry. In 1964, the Transit-5BN-3 mission was aborted because of a launch vehicle failure resulting in burn-up of the SNAP-9A unit. This resulted in dispersal of plutonium fuel in the upper atmosphere. Following the event, RTG design philosophy was revised to "survival during orbital reentry."[1,2]

The second generation fuel form was based on plutonium-oxide-molybdenum cermet. A ceramic-metallic mix, this fuel form survived a failed launch attempt in 1968 and was recovered intact on the seabed in 300 ft of water off the coast of California.[3]

To improve efficiency of thermal-to-electric power conversion, the fuel form was changed again to a pure plutonium-oxide ceramic in the early 1970s. The ceramic permitted higher operating temperatures than the moly-cermet. All RTGs since 1975 have used a plutonium-oxide ceramic. The original ceramic, the multi-hundred watt heat source, was based on a spherical geometry. This was quickly replaced by the GPHS. GPHS improvements over fuel sphere assemblies (FSA) or earlier fuel forms includes survivability characteristics, especially containment after an accident, modular design, and higher power density. This design is still in use today and is the heat source for most new RPS concepts.

2.2 Facilities

The Savannah River Plant began producing Pu-238 in the late 1950s by irradiating Np-237. Approximately 300 kg were produced between 1959 and 1988. Two kilograms of high purity material, containing 0.3 ppm Pu-236, were produced in 1970–73 for medical applications. This material was produced by irradiating Am-241 to produce Cm-242, which then alpha decayed to Pu-238. In 1961, Building 235-F was converted to produce Np-oxide-alum targets for irradiation in the reactors. The target design evolved into thin tubes fabricated in the 321-M building. Separations were initially performed in the high-level caves. The process was scaled up and mounted onto frames installed in the 221-H canyon.[4]

Initially, oxide powder was shipped to the Mound Plant in Miamisburg, Ohio, for fabrication into heat sources. Mound dissolved the delivered oxide powder and reprecipitated it as hydroxide $Pu(OH)_3$. The hydroxide cake was passed through a sieve to produce granules that were heat treated to form the oxide and hot pressed.

In September 1971, the Atomic Energy Commission (DOE's predecessor) made a decision to transfer plutonium molybdenum cermet fuel form preparation from the Mound facility to Building 235-F at the Savannah River Site (SRS). The decision was made out of concern about continued processing of plutonium powder at Mound in proximity to a significant population center. SRS was chosen because of (1) its remoteness from population centers, and (2) the availability of Building 235-F, the use of which would result in a substantial savings in construction costs for a new facility. To eliminate the need for transporting Pu-238 powder in the public domain, iridium encapsulation of the pure plutonium oxide (PPO) spheres was also transferred to the Plutonium Fuel Fabrication Facility (PUFF), constructed within Building 235-F.

Construction of PUFF began in October 1973 and was completed in mid-July 1977. Production of iridium-encapsulated 100-W Pu-238 spheres for multi-hundred watt RTGs commenced in 1978 and was completed in April 1980. In June 1980, production of the 62.5-W GPHSs for NASA's Galileo and Ulysses missions began. By December 1983, all heat source production was completed for these missions. The last heat sources were shipped to Mound in February 1984 for final assembly. During production, PUFF processed approximately 165 kg of Pu-238. When production was completed, the PUFF facility was placed in standby mode.

Because of the presence of corrosive Pu-238 in the PUFF process cells, many systems, including ventilation and manipulators, failed while in standby. Failure of the ventilation system allowed moisture into the cells, accelerating corrosion. These systems were intentionally left in disrepair because the corrosive nature of Pu-238 would attack the repaired systems, causing repeated failures.

When it was time to restart PUFF, extensive damage had occurred while in the standby mode resulting in increased costs and time to refurbish the facility. These conditions made it necessary in 1990 for DOE to transfer heat source production responsibilities to Los Alamos National Laboratory (LANL) for the Comet Rendezvous Asteroid Flyby and Cassini space missions.[5]

LANL has aided in Pu-238 heat source development since the 1970s and began GPHS production in 1990. LANL produces Pu-238 pellets using the same methods that SRS used for processing and pressing oxide into pellets. Operations to produce Pu-238 heat sources are performed in the PF-4 facility at TA-55 at LANL. The pellets are encapsulated in iridium cladding. Up until 1997, the clad pellets were shipped to Mound, where they were assembled into heat sources and installed into the RTG. After completing assembly, Mound conducted final acceptance tests, and packaged and shipped the finished generator to the launch site.

In 2002–3, Mound Plant assembly and test operations were moved to the Idaho National Laboratory (INL). The decision to relocate these operations from Mound to INL was again based on the remoteness of the new facilities from population centers and the enhanced security posture necessary after September 11, 2001. This facility history including mission timeframes is summarized in Figure 2-1.

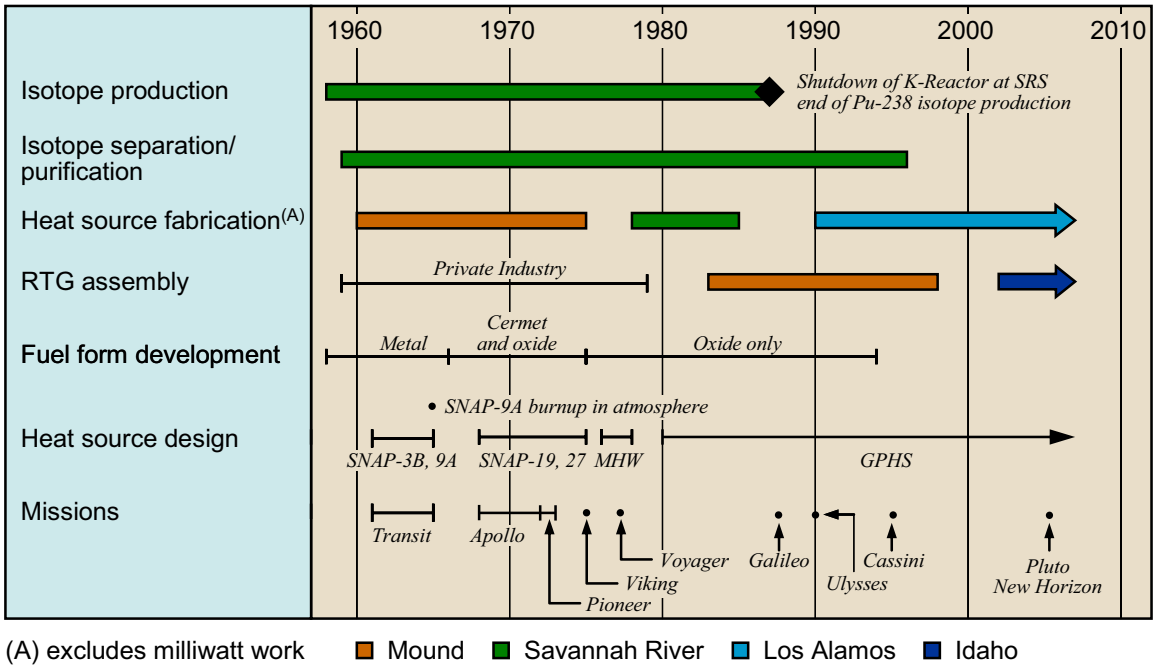


Figure 2-1. Timeline for Pu-238 development.

2.3 Baseline Process

All handling of unencapsulated $^{238}PuO_2$ is performed in gloveboxes. All processing gloveboxes are provided with inert gas, argon or helium atmospheres. Gloveboxes are attached to one another via vacuum/inert gas airlocks. Thus, if any glovebox is breached, the atmospheres of neighboring boxes are not affected.

The production of GPHS pellets ready for encapsulation from raw feed powder may be separated into 10 characterization and processing steps. [6,7,8,9] These steps are shown in Figure 2-2 and summarized below. As shown in the figure, the steps can be grouped into two subprocesses—granule production and pellet production. This grouping is used for evaluating alternative technologies. Additional detail on the individual process steps including equipment descriptions is included in Appendix B.

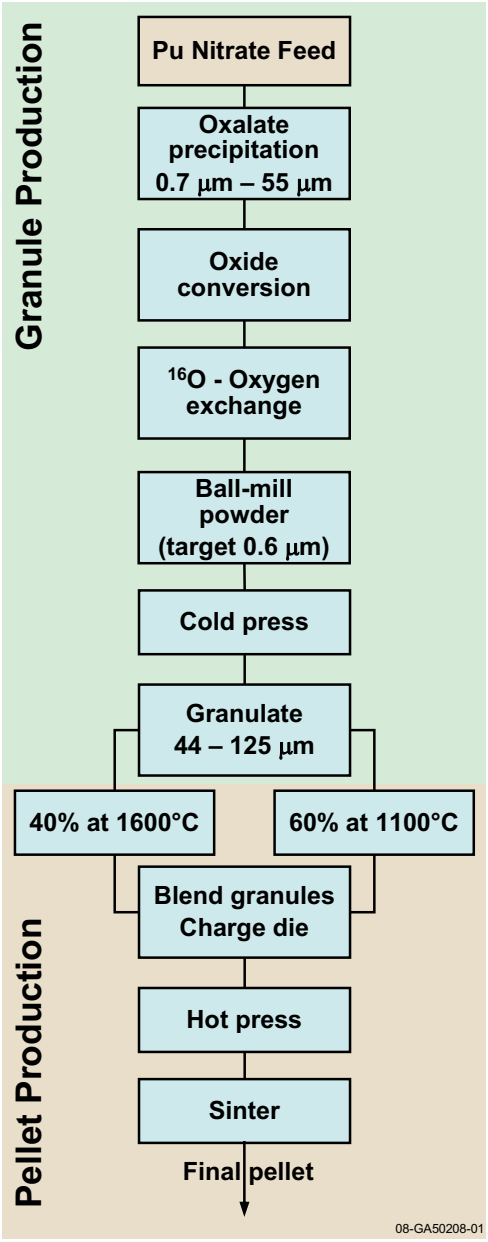


Figure 2-2. Current GPHS process flowsheet.

Oxalate Precipitation

The input stream to the pellet production process is plutonium-nitrate in an aqueous solution. The first processing step is to adjust the valence state of plutonium and blend with oxalic acid to precipitate plutonium oxalate. The plutonium material precipitates in rosette- and lath-shaped structures. The size of the precipitate varies from 0.7 μm to 55 μm. The material is collected on a metal filter at the bottom of the precipitator, which can be disconnected from the precipitator and transferred to a furnace for further processing.

Oxide Conversion

The second processing step involves heating the oxalate precipitate driving off any remaining moisture. Nominal furnace temperature during calcining is 735°C.[10] This dries the plutonium oxalate precipitate and converts the plutonium oxalate precipitate to plutonium-oxide, PuO_2.

Oxygen-16 Exchange

Next, the as-received feed powder is heated in an O-16 environment to replace the O-17 and O-18 isotopes present in the feed with O-16. The feed powder produced with natural oxygen has a neutron emission rate in excess of 17,000 n/s-g ^{238}Pu,[7] primarily owing to (α,n) reactions caused by the presence of O-17 and O-18 isotopes in the normal oxygen used in calcining operations. The exchange is accomplished by heating a platinum boat, filled with the appropriate amount of feed powder, in a furnace in an atmosphere of flowing Ar saturated with $H_2{}^{16}O$. The material is heated to 775°C for 24 hours.[7]

Ball Milling

Ball milling the feed powder is required to produce the desired particle size and powder morphology. This is, to some extent, a normalizing step to eliminate differences in surface activities and powder packing from one lot of feed powder to the next. The as-received powder consists of two types of particles and has a mass-median diameter of about 2.7 µm. Data during the Cassini program showed mass-median particle size of 20 µm. One type of particle is rosette-shaped; the other is lath-shaped. The lath-shaped particles have an extremely high surface activity, low packing density and cause the material to shrink excessively when sintered. The results of developmental studies show the reactivity of the feed will be adequate for bonding during hot pressing if the powder is milled to produce a mass-medium diameter of about 1 µm.[7]

Cold Press and Granulate (Slugging and Screening)

The slugging and screening operations are performed to convert the ball-milled powder to granules of the size desired for hot pressing. The plutonia powder is cold pressed at 400 MPa to form a green pellet at 60% theoretical density (TD). The pellets are then broken and screened to size and the <125 µm fraction is collected. Movement of the ball-milled material and the screening operations are performed manually. These operations spread the most contaminated dust within the gloveboxes.

Granule Seasoning

This is the most important prepress processing step. After the <125 µm granules are made, they are thermally seasoned to form the reactive and nonreactive components of the grog-feed mixture. The majority of the green granules, 60 wt%, are seasoned for 6 hours at 1100°C in flowing Ar-$H_2{}^{16}O$. The remaining granules, 40 wt%, are seasoned for 6 hours at 1600°C.[7] After seasoning, the granules are screened again through a <212 µm mesh. Heating and cooling rates for both seasoning operations are 300°C/h. Seasoning the granules in Ar-$H_2{}^{16}O$ prevents the back exchange of the O-17 and O-18, and frequently leads to a further reduction (5 to 10%) in the neutron emission rate.

The most important parameter in processing the feed before hot pressing is the temperature at which the reactive component of the grog mixture is seasoned. If the temperature is too low, granules will be too reactive, leading to excessive shrinkage and crack formation when the pellet is postpress sintered. If the temperature is too high, the granules will not be reactive enough to form around the nonreactive high-fired granules to produce a homogeneous microstructure. Thus, it is imperative that the temperature profiles be determined accurately for the furnaces and that temperature control and measurement systems be in good working order.

Blending and Die Loading

The grog-type feed used to fabricate the GPHS fuel pellets is obtained by mixing the proper ratio of <212 µm granules seasoned at 1100°C (60 wt%) and 1600°C (40 wt%). The mixing is accomplished by putting the granules into a blending jar and rolling it without any grinding balls. After the mixing is completed, the graphite hot pressing die is charged with approximately 150 g of the granule mix.[7]

Hot Pressing

The GPHS pellets are pressed one at a time in the hot press assembly. After the die is positioned in the press, the system is evacuated to a vacuum chamber pressure of 13 Pa. A slight preload is initially applied and the material is preheated to 1300°C. After preheating, the programmed load cycle is initiated. The full programmed load for GPHS pellets, 20.5 MPa for 18 minutes, then 20.9 MPa for 9 minutes, is attained in 8 to 9 minutes from the initiation of the load cycle. The die is held at 1500°C during the full load.[7] At the end of the pressing cycle, the heater is turned off and the load is removed from the die assembly. The chamber is allowed to cool for about 1 hour and then the vacuum system is valved off and dry argon is introduced into the chamber to facilitate cooling. After the suitable cooling period, the vacuum can is raised and the die assembly is removed.

Postpress Sintering and Pellet Storage

After the pellet is removed from the die insert, it is stored in a graphite container for 16 hours or longer (overnight). Pellets sit for as long as 2 weeks before sintering with no obvious deleterious effects. After storage, the pellet is weighed and the dimensions are measured. The pellet is then sintered in flowing Ar-$H_2{}^{16}O$ for 6 hours at 1000°C followed by 6 hours at 1527°C. During the sintering operation, the pellet dimensions will shrink by about 0.5 to 0.8%.[7]

During hot pressing, the plutonia is reduced to a stoichiometry of about $PuO_{1.88}$. The pellet is stored overnight so that it will be reoxidized to $PuO_{2.0}$ or nearly so before the dimensioning activities. Similarly, the Ar-$H_2{}^{16}O$ gas flow is started before the furnace is turned on to ensure a stoichiometry of $PuO_{2.0}$ before the pellet is sintered. The use of Ar-$H_2{}^{16}O$ flow gas precludes back exchange of O-17 and O-18 and subsequent increased neutron emission rates.

2.4 Lessons Learned from Baseline Process

The radiologic difficulties with the oxalate-based granulation process were controlled in the experimental facilities at SRS through fastidious cleanup of spilt or airborne-deposited powder. However, in the SRS Pu Fuel Fabrication Facility, the large cells and gloveboxes restricted the ability to remove deposited material. As a result, it was necessary to schedule glovebox glove changes often at some locations to prevent premature glove failures and radioactive release to occupied areas. At the completion of SRS heat source fabrication, the processing incident data base for Pu-238 and Pu-239 operations were compared. It was concluded the overall probability of an incident was proportional to the amount of radioactivity processed (curies) rather than the mass of material processed. Thus, the probability of an incident with Pu-238 was about 200 times more likely per gram of powder than it was per gram of Pu-239.

The granulation and pelletization operations at LANL and SRS are manual activities. As a result, radiation doses to operators are generally proportional to the amount of material processed, and to the amount of residues in equipment during maintenance operations. Any recycled material increases radiation doses because it is processed, prepared for reuse, and subsequently reused.

With this process, the main cause of the need to recycle material is pellet loss resulting from cracking. Pellet transfers between operations are major sources of fracture. Observation of the surface of the pellets indicates that hairline cracks are common after post hot pressing heat treatment. Fracture is believed to result from several causes. First, the decay heat of a normal pellet results in a temperature gradient across the pellet. Under enclosed storage conditions the average temperature of a pellet will increase from accumulated decay heat. Upon changing the surroundings of a pellet, thermal shock can occur from coming in contact with materials at a different temperature.

It is believed that one of the largest causes of cracking is phase changes resulting from shifts in the oxidation state of the plutonia pellet: During hot pressing, the plutonium dioxide reacts with the graphite die material containing it (carbothermic reduction). The resulting substoichiometric plutonium dioxide undergoes a volume change, creating stresses. Upon reoxidation, additional stresses occur. The resulting flaws in the pellets create weak points, making them more susceptible to thermal shock or mechanical forces during transfers.

2.5 Recent Programmatic History

As shown in the first two lines of Figure 2-1 above, production capabilities (irradiation in a reactor and isotope separation/purification) ceased approximately 20 years ago. There have been several abortive attempts to restart Pu-238 production at Hanford (1987–88, 1991–93, 1998–9) using the Fuels and Materials Examination Facility and Fast Flux Test Facility, at the Idaho laboratory (1998–2001) using a new facility and the Advanced Test Reactor, and at Oak Ridge National Laboratory (ORNL) (1994-2003) using the Radiochemical Engineering Development Center and High Flux Isotope Reactor/ INEEL-Advanced Test Reactor. Each design proposal was left unfunded and current planning is on hold. It is important to reestablish production capability in support of NASA and national security initiatives. The findings within this report should be considered for any new facility constructed for GPHS pellet fabrication.

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3. SAFETY AND HEALTH CONSIDERATIONS

Personnel working with plutonium are exposed to external gamma rays, x-rays, and neutrons, as well as possible internal exposures from uptakes as a result of upset conditions. The external radiation hazards are significant and are reduced to as low as reasonably achievable by reducing the time personnel are exposed to radiation fields; increasing distance from the radioactive material and personnel; using shielding to reduce intensity of the radiation; and reducing the radiation source term through appropriate decontamination. The internal radiation hazard results from alpha radiation emission and the high specific activity of Pu-238, which results in higher doses from smaller quantities of material than radionuclides having longer half-lives.

3.1 External Hazard

The external radiation hazard from Pu-238 consists of photons and neutrons. Photons are generated as a result of the decay of constituent radionuclides and their daughter products. They are generated during spontaneous fission events, may be present during the generation of neutrons during alpha interactions, and include Bremsstrahlung from the interaction of beta radiations. Neutrons are generated through spontaneous fission and through alpha interactions with the nucleus of lighter elements. Control of worker dose from external radiation during the handling of Pu-238, while challenging, has been successfully accomplished within the DOE complex. Dose rates from the fully assembled radioisotopic thermoelectric generator F-5 were measured in 2005 and are presented in Figure 3-1 as an example of actual dose rates encountered from Pu-238.[1]

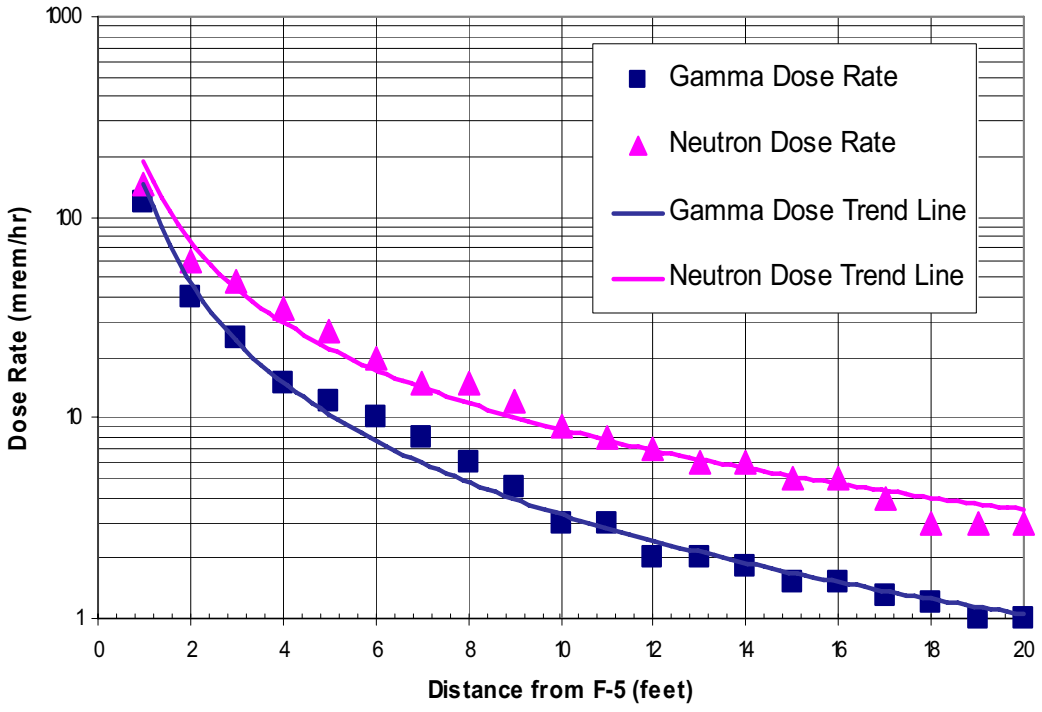

Figure 3-1. RTG F-5 radiation dose rate.

3.2 Internal Hazard

Experience in the nuclear industry has shown that the most likely route of accidental internal exposure to workers is by inhalation. Other routes include ingestion and injection. For the plutonium oxide used to create heat sources, these other routes of entry usually result in much lower dose than the inhalation route. Inhalation has been evaluated for absorbed radiation dose to the respiratory tract, and the respiratory tract as a portal of entry of plutonium to the blood.

A very small quantity of material if inhaled would exceed federal regulatory limits. The annual limit on intake for Pu-238 inhalation is 4×10^{-8} Ci.[2] This is equivalent to approximately 2.7×10^{-9} g of Pu-238 oxide. A single particle of fully dense plutonium oxide having this activity would have a physical diameter of approximately 8 µm. Its equivalent aerodynamic diameter would be about 27 µm. So it would take only a few particles in the respirable range to exceed the federal regulatory limit for annual exposure. The high activity per particle for Pu-238 makes it difficult to control personnel dose during airborne events. As shown in Figure 3-2, the current precipitation process and ball milling operations produce material in the most hazardous size for inhalation.

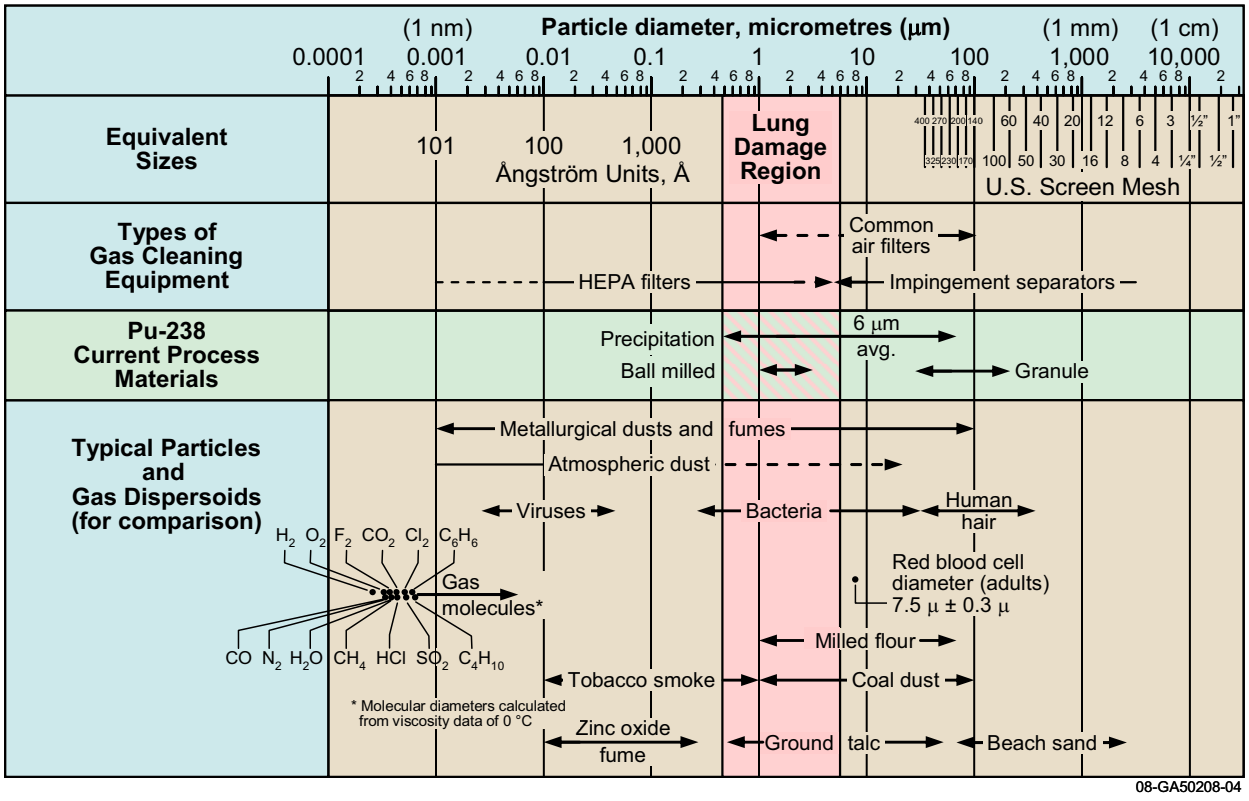

Figure 3-2. Comparison of Pu-238 particle size to respirable materials.

While engineered barriers (containment, ventilation, etc.) are used to reduce the possibility of personnel coming into contact with airborne plutonium particles, additional reductions would be gained by choosing manufacturing techniques that minimize the generation of fine particles and reduce human interaction.

3.3 Plutonium Accidents

The following accident summaries obtained from DOE investigating team reports illustrate the radiological consequences that can result from working with Pu-238.

3.3.1 Glovebox Piping Failure[3]

On March 16, 2000, a supervisor performing his morning walkdown of glovebox lines in the Plutonium Processing and Handling Facility (PF-4) of the LANL Technical Area-55 (TA-55) noted that one glovebox had no argon flow through its oil bubbler. This inert glovebox has an argon atmosphere, maintained by a system that provides argon to the glovebox when its pressure falls below a specific setpoint and by an oil bubbler that regulates negative pressure.

The supervisor asked an electrical/mechanical technician to determine why there was no bubbler flow. Unknown to both employees, an electrical circuit providing power to the automatic argon control system had tripped, closing the argon solenoid supply valve.

In early afternoon, the technician began his maintenance evaluation to determine why the argon flow to the bubbler had ceased. Seven other workers were in the room. While the technician was examining the piping under the west side of the glovebox, alpha radiation hand monitors in the vicinity alarmed. Shortly after, the continuous air monitors in the four corners of the room also alarmed. All eight personnel immediately left the room.

The accident investigation board determined the direct cause of the accident was a release of airborne contamination from a leaking compression fitting in an inadvertently pressurized dry vacuum line. The vacuum line serves as an airlock between the glovebox and an adjacent dropbox.

Seven of the eight workers received confirmed intakes of Pu-238. The committed effective dose equivalent (CEDE) to the most affected worker may be as high as 300 R. Committed effective dose equivalent is an estimate of the 50-year radiation dose to an individual from radioactive material taken into the body through either inhalation or ingestion. Three workers probably exceeded their annual exposure limit of 5 R. Biological samples from the remaining workers showed significantly lower exposures. The four workers with the highest radiological intake began chelation therapy immediately.

3.3.2 Plutonium Storage Container Failure[4]

On August 5, 2003, two employees were conducting a preinventory check of accountable packages stored in Room 201B in the LANL Plutonium Processing and Handling Facility. The packages contained residues from stored Pu-238 awaiting further processing. The work required that the employees gain access to a shelving unit, referred to as a “cage,” behind portable radiation shielding and attached to the wall for seismic restraint. The employees were to remove individual packages in the cage and verify the packages’ identification numbers against an inventory listing. Once the numbers were verified, the packages would be returned to their position in the cage.

During this check, the continuous air monitors alarmed. Employees left the room immediately. The employees had not observed anything before the alarm, such as a visible defect on the exterior of the packages. Nor did they drop or otherwise mishandle a package. When the employees checked themselves and found they had been contaminated, they summoned a radiological control technician for assistance. Both workers had detectable levels of external contamination to 50,000 dpm alpha and their nasal smear results indicated potentially significant intakes of Pu-238. Initial dose estimates based on the nasal swipes suggested that the radiation doses could be in excess of 10 R CEDE. After a series of bioassays, the dose to the two workers was determined to be 3 R and 1.8 R CEDE.

The investigation concluded that the release of airborne contamination from a degraded package containing cellulose material and Pu-238 residues had caused the accident. The package had been stored in the room since 1996, and chemical, radiolytic, and thermal decomposition of the contents and the packaging materials had resulted in significant corrosion and gas generation. Each of these storage packages has three boundary layers: (1) an inner can, (2) a polyvinyl chloride plastic bag, and (3) an outer can. Corrosion had caused the two inner packages to fail and release their contents into the outer package. The corrosion also caused the leak path in the outer package to seal, resulting in a buildup of gas pressure within the outer package. Simply handling the package dislodged the corrosion at a junction between two seams in the outer can, and contaminated gases vented to the room. The investigation concluded the phenomena involved in the failure of the three boundaries were consistent with previous failures that had been observed during storage of plutonium. Therefore, this failure did not represent a unique or unexpected condition. The accident curtailed operations for eight months, during which time sponsor deliverables were not met.

3.4 References

1. Personal conversation between D. L. Atwood and L. L. Burke, September 2005.
2. EPA 520/1-88-020, “Limiting Values of Radionuclide Intake and Air Concentration and Dose Conversion Factors for Inhalation, Submersion, and Ingestion,” September 1988.
3. Type A Accident Investigation of the March 16, 2000 Plutonium-238 Multiple Intake Event at the Plutonium Facility, Los Alamos National Laboratory, July 2000.
4. Type B Accident Investigation of the August 5, 2003 Plutonium-238 Multiple Uptake Event at the Plutonium Facility, Los Alamos National Laboratory, December 2003.

4. MATERIAL REQUIREMENTS

Before alternatives to the baseline process can be developed, the end product must be clearly understood. This section addresses the material requirements including isotopic, fuel form, and construction. A number of assumptions were made to focus the alternatives for this study.

- Only the isotope Pu-238 will be considered as a fuel source for this evaluation.
- Only material in an oxide form will be considered.
- Only a GPHS pellet geometry will be considered. When considering the cost and time investment spent in developing the GPHS design (estimated at $40–$50 M over 5–8 years during the 1970s), alternate heat source designs are beyond near-term application.

4.1 Material Requirements

The material specification requirements for GPHS heat sources have not changed significantly since the 1970s. Comparison between the material specifications for Galileo,[1] Ulysses,[1] Cassini,[2] New Horizons and flight-quality GPHS[3,4] show they are essentially the same. Salient material portions from the specification are summarized in Table 4-1.

Table 4-1. Current GPHS material and product requirements.

Attribute	Requirement
Isotopic content	- greater than 82% Pu-238 - less than 2 µg/g Pu-236[a]
Actinide impurity	- less than 1 weight percent total content - less than 0.5 weight percent individual actinide impurity
Anionic impurity	- phosphorous content shall not exceed 25 µg/g
Cationic impurity	- less than 2,550 µg/g - less than 1,500 µg/g combined silicon, magnesium, calcium and aluminum[b] - *individual limits also exist but are excluded from this summary*
Granule size	- less than 125 µm
Neutron emission	- less than 6,000 neutrons/sec per gram of Pu-238[c]
Pellet geometry	- diameter of pellet shall be 27.56±0.23 mm - length shall be 27.56±0.38 mm - weight shall be 151.0 +0.7/-0.5 g
Thermal inventory	No requirement exists on the unencapsulated pellet. (Thermal energy is controlled by isotopic content above and verified after cladding)
Pellet integrity	Not required

a. The Pu-236 daughter products include Bi-212, and Tl-208, which produce moderate gamma radiation.[5]
b. The impurities can affect performance by volatizing, transporting to, and plugging vent openings. Also, impurities can interact with iridium and lead to cladding embrittlement and or failure.
c. Neutron radiation is deleterious to equipment and instrumentation of the satellite. Reduction in neutron emission is accomplished by reducing O-17 and O-18 content in the oxide. Slight differences in emission rates for exchanged lots can be attributed to lot-to-lot variations in the content of light element impurities that can cause (α,n) reactions.[5]

The quality and impact behavior of the finished pellet can be significantly altered by particle size, reactivity, and degree of sintering. In lieu of specifying all material parameters required to ensure a quality pellet, the approach has been to tightly control the process to ensure consistency between new batches and the original product, i.e., the end product is the same if made the same way every time. Therefore, current specifications dictate process parameters in addition to material specifications. Requirements that are process-specific are summarized in Table 4-2.

Table 4-2. Current GPHS process requirements.

Attribute	Requirement
Seasoning	- 60% of the granules shall be seasoned for 6 hr at 1,100ºC in flowing argon saturated with $H_2{}^{16}O$
	- 40% of the granules are seasoned for 6 hr at 1,600ºC in flowing argon saturated with $H_2{}^{16}O$
Pressing	- the graphite die geometry is specified by drawing
	- pellet is hot pressed in vacuum at 2,750 lbf for 18 min and then 2,800 lbf for 9 min at 1,500ºC. The vacuum is less than 0.1 torr at the start of pressing
Postpress	- pellet is sintered in flowing argon saturated with $H_2{}^{16}O$ for 6 hr at 1,000ºC, followed by 6 hr at 1,527ºC.

4.2 Target Material Attributes

As explained in the current process description, the heat source fabrication process can be divided into two subprocesses—granule production and pellet production. To develop a new process (and evaluate process alternatives), researchers made an effort to define the material parameters of products from the granulate production and pellet production subprocesses defined in Section 2.3 because target parameters for the granule formation have the greatest influence on the finished pellet, researchers estimated the material parameters of the granule based on a reverse engineering approach. In this report, these parameters are considered target material attributes. Through testing and refinement, these attributes could evolve into new material specifications for heat sources.

The target material attributes are based on the current process and research to date:[5,6,7] Table 4-3 lists target attributes for green granules. This material is midway through the fabrication process before seasoning. Experimental evidence indicates the prepress seasoning temperature is the overriding factor in attaining high densities and well-ordered structures.[8]

Table 4-3. Target granule material attributes.

Attribute	Requirement
Granule size	- 60-125 µm[5,6 a]
Granule geometry	- Spherical shape with large surface area ratio.[6]
Granule density	- High-fired material density greater than 95% theoretical density.[6]
	- Low-fired material density–**Data does not exist.**[b]
Tap density	- Recommended tap density is inconclusive from test reports
	- 1.9–2.3 g/cc[9] (was optimal for precip mat'l in current process)
	- 4.0 g/cc[7,10]
	- SRS Lot 27, Run 113, with tap density 4.0g/cc was not sufficiently close to GPHS granulated feed to fit in the die for pressing[11]
	- **Data on pour and tap density of granules from the current process does not exist.**[b]
Fines production	- Minimize fines, prefer less than 5%.

a. Optimal granule size may vary depending on the pellet fabrication method.
b. Based on discussions with LANL, granules have not been characterized to obtain this data.

Table 4-4 lists the target attributes of the finished unclad pellet. While many pellets are easily quantified, impact response behavior is not. The optimal fragment size resulting from an impact is inconclusive from text reports. Clad failure apparently becomes probable whenever the fuel breakup and external capsule support permit large fuel fragments to move across one another. Capsule survivability appears to improve when the fuel is modified such that breakup into large fragments is unlikely.[12] The differential displacement and subsequent pushthrough of large fuel fragments caused the failure of one safety verification test (SVT) -12 primary clad (FC-628). Extensive fuel breakup caused the failure of one SVT-12 secondary clad (FC-226). The impact apparently broke the fuel into fragments that permitted excessive clad deformation and forced the trailing face of the capsule to stretch. The failure occurred as a result of the simple stress overload.[13] Some researchers postulate that the material property fracture toughness may be useful in predicting impact behavior. Correlation of fracture toughness with impact response can be investigated as part of a process development test program.

Table 4-4. Target attributes of the finished unclad pellet.

Attribute	Requirement
Grain size	- Average grain size of finished pellet >10, or 20-30 µm[9,10]
Theoretical density	- Max expected density without fracture–86%[11] - Nominal 82-86% functional range between 80-88%
Linear shrinkage	- From final heat treatment after pressing <0.5%
Impact response	- Minimize production of fines Recommended fragment size is inconclusive from test reports
Microstructure	- High density particles, greater than 95%, distributed in a matrix - Porosity evenly distributed throughout the pellet
Fracture toughness	To be developed by future experimental work. Expect value to be within a range. If too high, the pellet behaves as a slug punching through the cladding. If it is too low, the pellet behaves like a fluid (flowing sand) causing clad failure by excessive deformation.

4.3 References

1. *Product Specification-General Purpose Heat Source for Galileo/Ulysses*, CP47A14635, Martin Marietta Astro Space.
2. J. W. Barber, *Cassini Pu-238 Program Specifications for Plutonium Dioxide Powder for General Purpose Heat Source Fuel*, WSRC-TR-92-132, December l993.
3. D. F. Bickford, SRP, to R. S. Swingle II and E. O. Kiger, SRP, "General Purpose Heat Source (GPHS) Specifications," DPSP-79, 1076, January 14, l980.
4. Anastasia McLaughlin, *^{238}Plutonium Dioxide Fuel Pellet Specification for General Purpose Heat Source (GPHS)*, NMT9-AP-026, July 1995.
5. R. A. Kent, *LASL Fabrication Flowsheet for GPHS Fuel Pellets*, LA-7972, August l979.
6. Glenn A. Burney, James W. Congdon, *Direct Fabrication of $^{238}PuO_2$ Fuel Forms*, DP-1621, July 1982.
7. J. W. Congdon and J. E. Marra, SRP, to C. R. Goetzman, SRP, *Initial Demonstration of Direct Fabrication Flowsheet for the Production of Pu-238 GPHS Pellets*, DPST-89-275, January l989.

8. T. K. Keenan, R. A. Kent, and R. W. Zocher, *The Relationship of Fabrication Parameters to Selected Properties of $^{238}PuO_2$ Radioisotopic Fuels. 1. Dimensional Changes, Stoichiometries, and Microstructural Features*, LA-5622-MS, May 1974.

9. Savannah River Laboratory Monthly Report, *^{238}Pu Fuel Form Processes*, DPST-75-128-8, August 1975, pg. 24.

10. Savannah River Laboratory, *^{238}Fuel Form Processes Bimonthly Report*, DPST-79-128-3/4, March/April 1979, pg. 10.

11. Savannah River Laboratory, *^{238}Pu Fuel Form Processes Bimonthly Report*, DPST-79-128-5/6, May/June 1979.

12. T. G. George, F. W., Schonfeld, *General-Purpose Heat Source Development*: *Safety Test Program-Postimpact Evaluation, Design Iteration Test 5*, LA-10232-SR, December 1984.

13. T. G. George, D. Pavone, *General Purpose Heat Source-Safety Verification Test Series*: *SVT-11 through SVT-13*, LA-10710-MS, May 1986.

5. PROCESS ALTERNATIVES

As explained in the current process description, the heat source fabrication process can be divided into two subprocesses—granule production and pellet production. Various process techniques were identified that could be used to produce either granules or pellets. Table 5-1 lists the processes. Subsequent sections describe each process.

Table 5-1. Alternate processes considered for production of granule and pellets using Pu-238.

Granule Production Methods	Pellet Production Methods
Improved oxalate precipitation	Improved hot pressing
Ammonium plutonyl carbonate precipitation	Liquid phase sintering
Hydroxide precipitation	Reaction bonding
Modified direct denitration	Preforming and pressureless sintering
Granat flocculation	Spark plasma sintering
Resin bead loading and calcining	Superplastic forming
Sol-gel microsphere	
Suspension/temporary binder	

The key to improving GPHS pellet production is a consistent quality feed powder from the granule process. This statement applies to most of the ceramic fuel processes. A consistent feed would enable the fabricator to characterize the powder and develop process parameters. The fabricator could develop parameters with confidence that they will be applicable throughout production. This evaluation considers the type of granules produced, the size distribution, and the consistency of product to improve GPHS production.

5.1 Alternate Granule Production Methods

5.1.1 Improved Oxalate Precipitation Process

5.1.1.1 Introduction

In 1982, SRS proposed a simplified approach to manufacturing GPHS pellets they had developed in the PUFF. They proposed modifying the oxalate precipitation step to directly produce agglomerates of small PuO_2 crystals. The crystals would be heat treated and loaded directly into the hot press die to produce the final GPHS pellets. Forming the large agglomerates directly allowed the fuel fabrication process to eliminate three steps, decrease personnel exposure, and reduce the risk of contamination release. SRS developed the process on a small scale and demonstrated its practicality first on a full scale using 20% Pu-240—80% Pu-239 oxide material and then using $^{238}PuO_2$ powder. Though the SRS tests were marginally successful, more development is needed to fine tune process parameters.

5.1.1.2 Process Description

The current GPHS fuel fabrication process receives fine particulate PuO_2 powders that have particles (4 to 6 μm), which are not agglomerated. The process includes ball milling to reduce particle sizes to <1 μm, cold-pressing into compacts, and granulation to form hot press feed agglomerates. The ball-milling step produces very fine particles that potentially can be airborne. The improved oxalate precipitation process eliminates these three steps from the current GPHS granule production process. Figure 5-1 contains an improved oxalate precipitation process flowsheet, with some of the process parameter details. Note the lightly shaded boxes where the eliminated process steps took place.

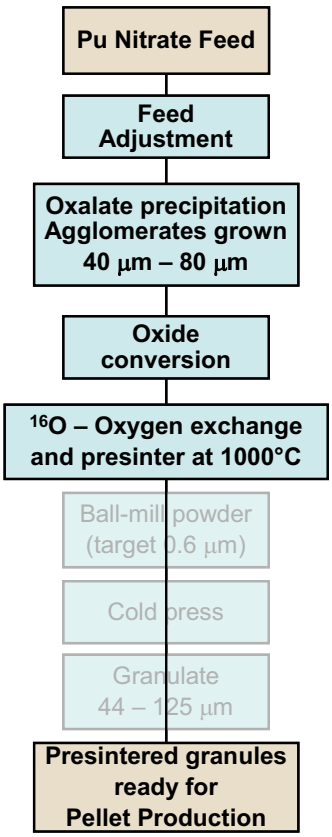

Figure 5-1. Improved oxalate precipitation.

5.1.1.3 Product Description

The improved process needs to produce large, 40 to 100 μm agglomerates strong enough to hold together during subsequent processing, and yet still contain an agglomeration of small crystals (particles 2 to 3 μm). This assures that during subsequent heat treatment and hot pressing there is sufficient activity to mildly densify and form final grain sizes ~10-20 μm. The granule agglomerates are shown in Figure 5-2.

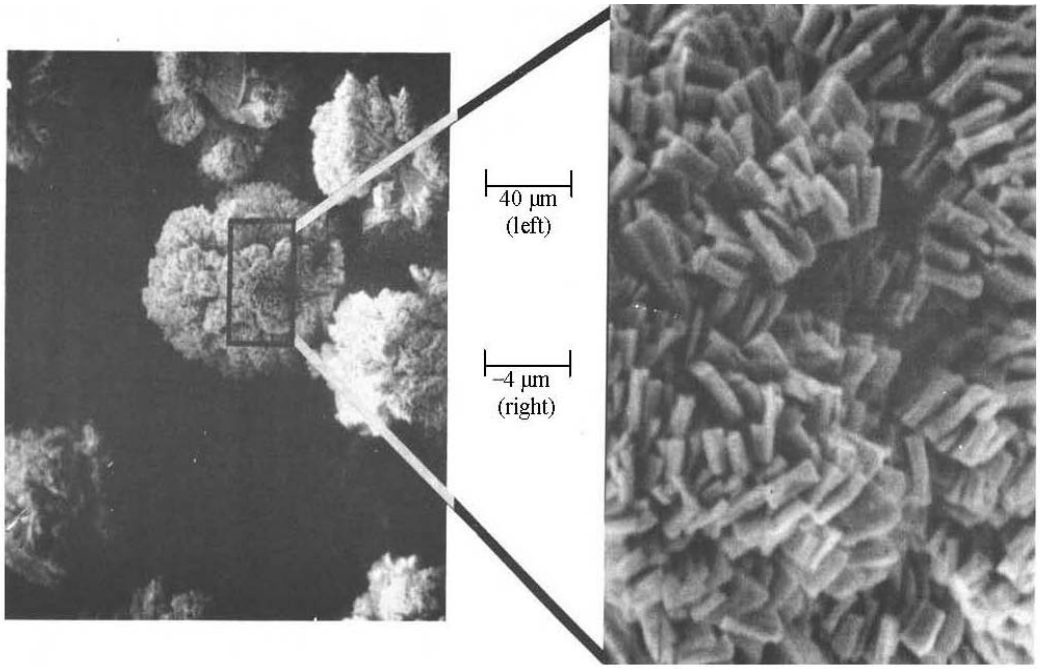

Figure 5-2. Rosettes (agglomerates) produced by improved oxalate precipitation.

5.1.1.4 Improved Oxalate Precipitation Reference

1. Glenn A. Burney, James W. Congdon, *Direct Fabrication of $^{238}PuO_2$ Fuel Forms*, DP-1621, July 1982.

5.1.2 Ammonium Uranyl Plutonyl Carbonate Precipitation

5.1.2.1 Introduction

Germany, Belgium and France investigated large-scale Pu-carbonate precipitation methods in the 1970s and early 1980s for spent nuclear fuel recycling.[1] The goal was to extract Pu from spent fuel and fabricate new mixed (uranium and plutonium) oxide fuel (MOX) fuel for Light-Water Reactor power production. Carbonate precipitation was particularly attractive for MOX production because the process allowed for coprecipitation of uranium and plutonium from nitrate feed streams. The most developed carbonate precipitation process is based upon the ammonium-uranyl-carbonate conversion process used for uranium fuel manufacturing. This process was modified for MOX production and is referred to the ammonium-uranyl-plutonyl-carbonate (AUPuC) co-conversion.[2]

5.1.2.2 Process Description

The ammonium-plutonyl-carbonate precipitation (APuC) process is summarized in Figure 5-3. As with all precipitation methods, valance adjustment and control of the precipitating species must be performed for ligand reaction of the precipitation reactant. For APuC, the plutonium valance state in nitrate solution is typically in the +4 state. For ammonium carbonate precipitation, Pu^{4+} nitrate is first oxidized to the Pu^{6+} using concentrated nitric acid as the oxidant. Gaseous ammonia and carbon dioxide are bubbled into the hexavalent Pu-nitrate solution contained in a precipitation vessel. The $(NH_4)_4PuO_2(CO_3)_2$ precipitate is collected on a metal frit filter and washed with 15% $(NH_4)_2CO_3$ and alcohol. The double carbonate decomposes to PuO_2 when dried in air at moderate temperatures.[3] The MOX product was calcined in reducing conditions at ~750°C to form a dense oxide.

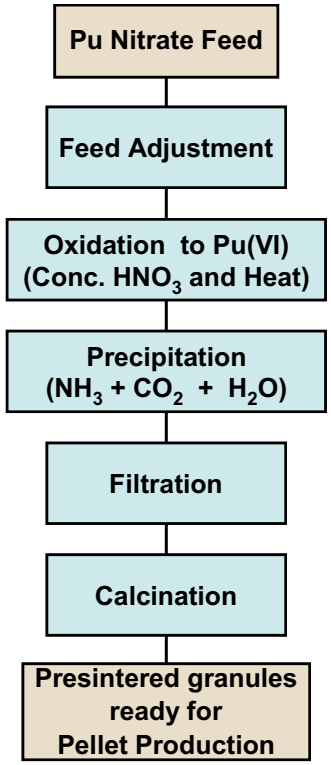

Figure 5-3. Plutonium-nitrate conversion to oxide by APuC.

5.1.2.3 Product Description

MOX production performed by the AUPuC method indicated that the oxide crystals were of moderate size with an average particle size of 50 μm, and 90% of particles were greater than 10 μm. The calcined oxide product had good sintering activity and produced dense free flowing powder. The Pu(VI) ammonium carbonate is not stable and decomposes in air to the monocarbonate.[3] This may be a potential issue in the high alpha and temperature environment associated with Pu-238 precipitation and oxide conversion. The sintered oxide product produced highly sintered, dense crystals with low porosity. Figure 5-4 shows a micrograph of the sintered oxide.

5.1.2.4 Process Characteristics

Process control is extremely precise owing to gaseous reagent flow control and mixing. Moderate-sized precipitate and oxide particles are produced, but so is a fraction of fine powder. The precipitate product was easily handled and filtered well, but is only moderately stable and decomposes in air with time. Proprietary technology exists for the MOX Pu(VI) ammonium carbonate process and is a proven method for MOX production.

Figure 5-4. $UPuO_2$ crystals produced by AUPuC fabrication.

5.1.2.5 Carbonate Precipitation References

1. H. Roepenack, F. Schlemmer, G. Schlosser, "KWU/ALKEM-Experience in Thermal Pu-Recycling," *International Atomic Energy Agency Specialists' Meeting on Improved Utilization of Water Reactor Fuel with Special Emphasis on Extended Burnups and Plutonium Recycling*, *1984,* NEACRP-L-275, CEN/SCK, *Mol, Belgium*.
2. V. Schneider, F. Hermann, W. G. Druckenbrodt, "The AUPuC process: A co-precipitation process with good product homogeneity to the full scale of plutonium concentration, ENC '79," *Transactions of the American Nuclear Society*, Vol. 31, pg. 176, 1979.
3. J. M. Cleveland, "Plutonium Conversion Processes," *Plutonium Handbook, A Guide to the Technology*, O. J. Wick, Ed., Chapter 15, Vol. I and II, American Nuclear Society Publications, 1980.

5.1.3 Hydroxide Precipitation

5.1.3.1 Introduction

Mound Laboratory fabricated the multi-hundred watt, PPO spherical heat source through the mid to late 1970s using $^{238}PuO_2$ granule material produced by hydroxide precipitation. Thus, of the precipitation methods, only the plutonium hydroxide (Mound) and plutonium oxalate (Savannah River Laboratory [SRL] and LANL) precipitation methods have been used to generate plutonium oxide heat sources used in flight applications. Mound Laboratory chose the hydroxide precipitation process because it was essentially dust free and produced granules that could be directly heat treated and hot pressed. SRL proposed to produce $^{238}PuO_2$ by hydroxide precipitation,[1] but chose the oxalate method instead.

5.1.3.2 Process Description

Plutonium (III) and (IV) readily form precipitates of $Pu(OH)_3$ and $Pu(OH)_4$, respectively, in the presence of hydroxide ion. Plutonium hydroxide precipitate formation is very effective because of the extremely low solubility of Pu(IV) hydroxide precipitate product[2]:

$$[Pu^{4+}][OH^-]^4 = 7 \times 10^{-56}.$$

The hydroxide precipitation process is generally nonselective with the formation of other cationic hydroxide precipitate species in addition to Pu hydroxide; therefore, the plutonium feed solution must be of high purity. The process can be performed either by direct strike (hydroxide added to Pu nitrate solution) or reverse strike (Pu nitrate solution added to hydroxide) to form the

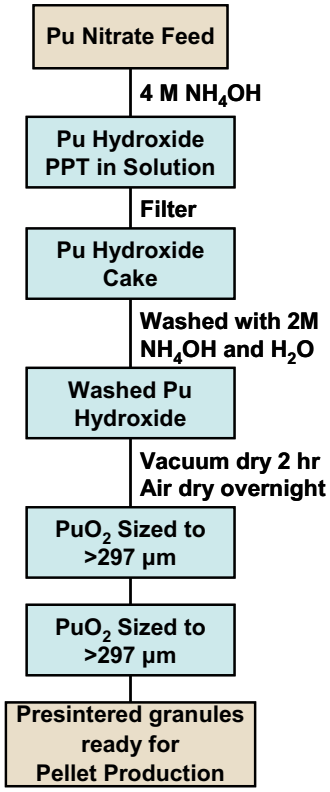

Figure 5-5. Mound Laboratory Pu-238 hydroxide precipitation and oxide conversion process.

hydroxide precipitate. The Mound Laboratory process[3] to convert Pu-nitrate solution to the oxide is shown in Figure 5-5. The Mound process involved feeding Pu(IV)-nitrate solution to a precipitator containing 4M ammonium hydroxide (reverse strike method). The $Pu(OH)_4$ precipitation was collected as a "cake," then filtered and washed with an ammonium hydroxide solution and water. The Pu hydroxide cake was vacuum dried, then dried in air to convert the product to a plutonium oxide cake. The $^{238}PuO_2$ cake is then crushed to produce shards of desired particle size, but with essentially no fine powder. A similar hydroxide precipitate process uses magnesium hydroxide to react with Pu nitrate solution[4]; however, for Pu-238 heat source applications, precipitation with ammonium hydroxide is preferred to minimize introduction of cationic impurities. Once the oxide had been sized, the powder was sintered at 1200°C and oxygen isotope exchanged with $^{16}O_2$ to reduce neutron emission. This powder was then hot pressed into approximately 1.5-in. spherical heat source units.

5.1.3.3 *Product Description*

Crushing of the $^{238}PuO_2$ cake product produced shard-shaped granules similar to those illustrated in Figure 5-6. For most heat source applications, the granules were sized to range between 53 to 250 μm in diameter after final sintering and with no fine powder.[5] After sintering, the granules were found to have open porosity with a density of approximately 10.2 g/cc or 89% theoretical density. The bulk powder density was generally determined to be 6.7 g/cc. Other thermodynamic, mechanical, electrical, chemical, and physical properties of this oxide material can be found in Reference 6. One disadvantage of the process involved handling and filtering of the Pu hydroxide cake material. The hydroxide is a sticky, gelatinous precipitate with a chemical formula of $Pu(OH)_4 \bullet xH_2O$ that is difficult to handle and filter. On the other hand, once the dried plutonium oxide cake was formed, handling, crushing, and sizing of the product was straightforward and dust free.

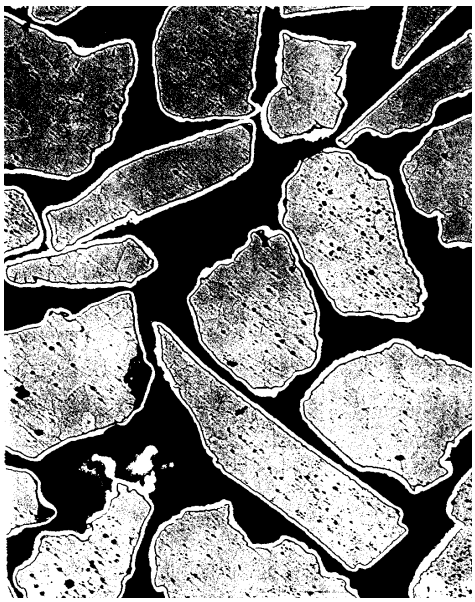

Figure 5-6. Pu-238 oxide shards with dimensions of 80 to 200 μm pressed in molybdenum cermet heat source, produced by plutonium hydroxide precipitation.

5.1.3.4 *Process Characteristics*

Plutonium-nitrate feed stream added to ammonium hydroxide allows direct precipitate formation and is a straightforward process. The $Pu(OH)_4$ precipitate is gelatinous and can be difficult to handle, but the resulting oxide cake allowed for granule production that was dust free. The plutonium oxide shard-shaped granules had an open porosity, a TD of approximately 90% and a reasonable packing density. After heat treatment, the granules were suitable for direct pressing. The plutonium nitrate stream must be of high purity as the hydroxide precipitation process is nonselective.

5.1.3.5 *Hydroxide Precipitation References*

1. G. A. Burney, M. C. Thompson, *Hydroxide Precipitation of ^{238}Pu*, DPST-72-433, 1972.
2. J. M. Cleveland, "Plutonium Conversion Processes," *Plutonium Handbook, A Guide to the Technology*, O. J. Wick, Ed., Chapter 15, Vol. I and II, American Nuclear Society Publications, 1980.
3. Mound Laboratory Pu-238 Heat Source Production Archived Records, "MHW PPO Sphere Fabrication Flowsheet," INL Archival Storage, Box 164971.
4. M. Jansky, *Radioactive Air Emissions Notice of Construction for the Magnesium Hydroxide Precipitation Process at the Plutonium Finishing Plant*, DOE/RL-99-77, 1999.

5. P. A. Teaney, *$^{238}PuO_2$ Fines Generation in Radioisotipic Heat Sources*, MLM–3069, 1983.

6. Mound Laboratory, "Plutonium-238 and Polonium-210 Data Sheets," MLM-1441, 1967.

5.1.4 Summary of Alternative Precipitation Methods

Table 5-2 categorizes positive and negative attributes of the alternative precipitation and oxide conversion processes described above. This categorization is somewhat subjective owing to the limited data available for comparing various methods and the lack of a more systematic study with experimental results.

Table 5-2. Attribute comparison of the described alternative precipitation methods.

Attribute	Direct-Strike Oxalate	Ammonium Carbonate	Hydroxide
Fine powder production	No	Minor- during precipitation	Minor- during granulation
Size distribution	Narrow	Wide	Narrow
Size control	Good	Good	Excellent
Product purity	Excellent	Excellent	Good- if feed is pure
Chemical reagent requirements	Low	Medium	Low
Process complexity	Moderate	Moderate	Moderate
Oxide product quality	Good- Rosettes of well bonded agglomerates	Moderate-polygonal crystals of various size	Moderate- broken shards

5.2 Alternative Conversion Methods

5.2.1 Denitration

5.2.1.1 Introduction

A number of denitration processes were evaluated for granule production. The processes evaluated were developed for UO_2 fuel pellet fabrication; therefore, they are not directly applicable to the Pu nitrate conversion to $^{238}PuO_2$ without further development. Some of the various denitration methods include the following:

1. NITROX, a freeze-drying method where denitration occurs under vacuum, was developed in France.[2]
2. Microwave decomposition, a batch denitration process, was developed by the Power Reactor and Nuclear Fuel Development Corporation of Japan.[3]
3. The modified direct denitration (MDD), developed at ORNL,[4] involves addition of an ammonium nitrate additive to form a 'double salt' precipitate, followed by conversion to oxide using a rotary kiln.

Of the various denitration processes described above, the MDD method using a rotary kiln appears to be the most applicable to conversion of Pu-238 nitrate solution to the oxide. The MDD is a very simple process and is easily applied at the scale needed for granule production. As discussed below, the process has also been demonstrated for mixed actinide (U/Np/Pu) conversion and with pure Pu with positive results.

5.2.1.2 Process Description

The MDD method involves adding ammonium nitrate (NH_4NO_3) to the Pu-238 nitrate stream to form the tetranitrate salt slurry. The slurry is then fed to a rotary kiln where the complex is decomposed and converted to the oxide in four distinct steps:

- Dehydration at 50°C
- Decomposition of the tetranitrate salt at 270°C
- Decomposition of the trinitrate salt at 300°C
- Conversion to the oxide at 500°C.

The decomposition and oxide conversion occurs continuously within the rotary kiln. The converted PuO_2 exits the kiln as a free-flowing powder. The MDD process is shown in Figure 5-7.

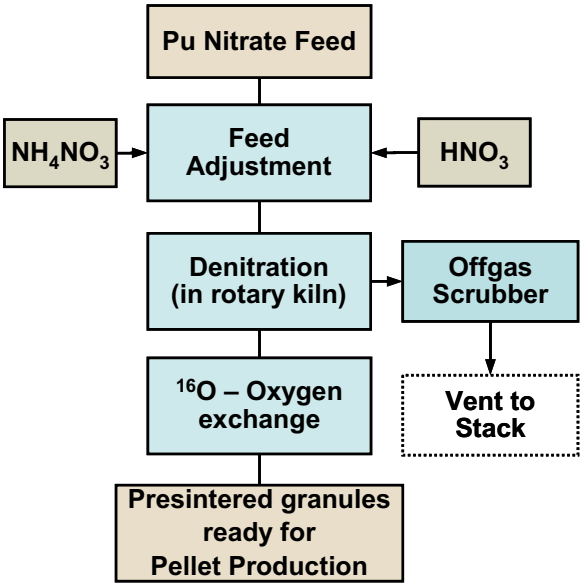

Figure 5-7. Process flow for denitration method.

5.2.1.3 Product Description

The MDD process has been developed for UO_2 fuel pellet fabrication, which aims to produce small oxide particles with large surface areas for enhanced sintering, resulting in high density, low porosity pellets. The oxide powder characteristics needed for $^{238}PuO_2$ heat-source pellet are quite different; therefore the MDD process will need to be tailored for this application. Because most development and demonstration activities have not been directed toward PuO_2, current literature does not fully evaluate the conversion process for application to $^{238}PuO_2$ heat-source fabrication. However, considering the various parameter components associated with the denitration process, it seems reasonable that larger particles could be produced.[5] Current investigations on MDD production of $^{239}PuO_2$ show good particle size distributions with the majority of material in the 180 µm particle size range and approximately 10% of particles below 38 µm (see Table 5-3). The MDD produced $^{239}PuO_2$ powder had a tap density of 3.0 g/ml and a bulk density of 2.2 g/ml, and a high active surface area of 5 to 15 m_2/g. A micrograph of the MDD produced $^{239}PuO_2$ is shown in Figure 5-8.

Table 5-3. Particle size distribution of Pu-239 and cerium oxide powders produced by MDD.[6]

	Weight %		
Particle size, µm	Sample P01 (SEM)	Sample P02 (SEM)	Cerium run (sieved)
≥710	29	26	37
180	57	52	40
75	7	9	14
≤38	7	13	9

5.2.1.4 Process Characteristics

A favorable process characteristic associated specifically with the MDD is use of a rotary kiln to produce a free-flowing powder that can be directly pressed into a pellet. Specialized and commercially available rotary kilns used specifically for fabricating ceramic oxides have multiple heating zones with atmospheric control that allow for the dehydration, decomposition, and oxidation to the final PuO_2 product in a single process. This ability to convert the initial liquid Pu nitrate state to the final Pu oxide state in a single process instrument with no intermediate handling has significant advantages in simplifying the conversion process of Pu-238 oxide production. However, current investigation of the MDD process has focused primarily on uranium oxide production with very few PuO_2 studies.

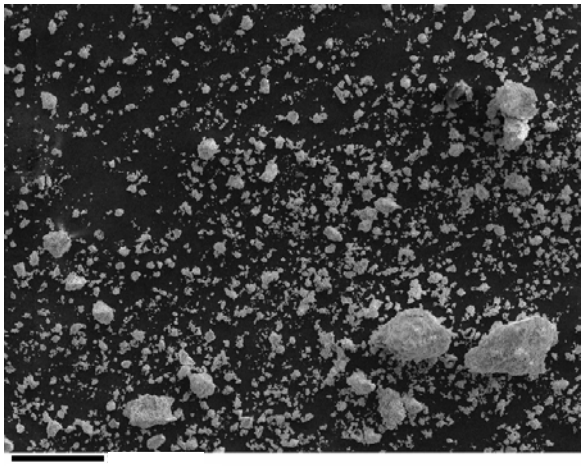

Figure 5-8. Scanning electron micrograph of Pu-239 oxide produced by MDD.[6]

5.2.1.5 Denitration References

1. P. A Haas, "A comparison of processes for the conversion of uranyl nitrate into ceramic-grade UO_2," *Nuclear Technology*, Vol. 81, pp. 393-406, 1988.
2. R. Romano, "NITROX Process: A Process Developed by COMURHEX of Continuous Denitration," *International Atomic Energy Agency Technical Committee Meeting on Advances in Uranium Refining and Conversion, Vienna, Austria, 1986*.
3. M. Koizumi, K. Otsuka, H. Oshima et al, "Development of a process for co-conversion of Pu-U nitrate mixed solutions to mixed-oxide powder using microwave heating method," *Journal of Nuclear Science Technology*, Vol. 20, No. 7, 1983, pg. 529.
4. P. A. Haas et al, *Development of Thermal Denitration to Prepare Uranium Oxide and Mixed Oxides for Nuclear Fuel Fabrication*, ORNL-5735, 1981.
5. L. K. Felker, R. J. Vedder, R. R. Brunson, E. D. Collins, "Plutonium and Neptunium Conversion Using Modified Direct Denitration," Eighth Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation Abstract, November 2004, Las Vegas, NV.
6. R. J. Vedder, private communication to B. D. Patton, Oak Ridge National Laboratory, 2004.

5.2.2 Granat Flocculation

5.2.2.1 Introduction

The Granat method for manufacturing MOX fuel pellets, named after the pilot commercial plant in PA Mayak, was developed in Russia as a "safe, very simple, efficient and reliable" method to prepare MOX feed powder granules that can be used directly in a standard cold press and sinter operation. The method was developed as a continuous process wherein uranium and plutonium are coprecipitated from a mixed nitrate solution through formation of ammonium diuranate and plutonium hydroxide precipitates with ammonia addition, and subsequently controlling granule formation using a flocculating agent. The resulting granules are converted to oxide MOX feed powder and prepared for fabricating MOX fuel pellets. All development was done up to pilot scale, and the design of a full-scale continuous production

plant was also completed. Several successful irradiation tests were completed to validate the in-reactor performance of fuel fabricated with the Granat method.

5.2.2.2 Process Description

The following Granat operations are set up in cascade arrangement so that material can be easily fed in a continuous manner. Figure 5-9 illustrates the basic Granat production plant process.

- Prepare a mixed uranium-plutonium nitrate solution with a heavy metal concentration of 100 g/L
- Introduce a concentrated ammonia solution for a one-stage coprecipitation of U and Pu hydroxides
- Flocculate by adding a 6% solution of polyacrylamide
- Form strong dense granules
- Separate granules from mother liquor using a vibration separator
- Dry granules at 100ºC in air
- Calcine granules in air to form stable oxide
- Size through vibration sifter.

5.2.2.3 Product Description

The calcined powder produced by the Granat process consists of large granules that are rounded in appearance and thus flowable, and has proven to be excellent automated press feed powder (see Figure 5-10). It contains no small particles <10 μm and is therefore clean to work with. Table 5-4 contains a summary of some of the final calcined powder characteristics.

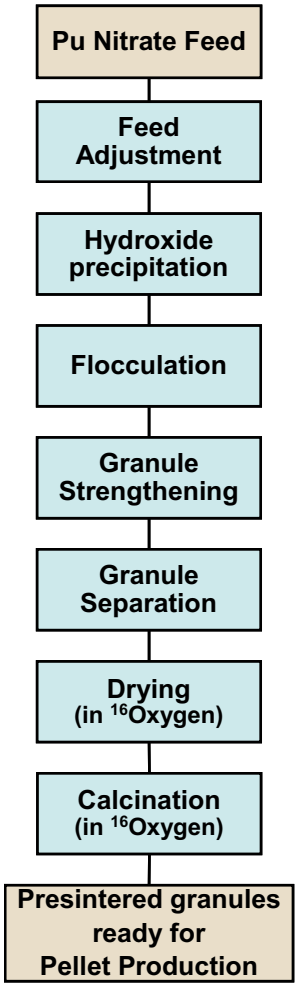

Figure 5-9. Process flow for Granat flocculation.

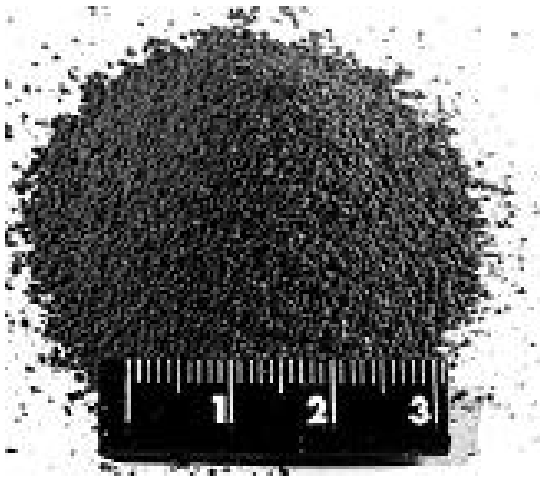

Figure 5-10. Calcined granules of MOX powder produced by the Granat process. (Scale in cm.)

Table 5-4. Granat calcined powder characteristics.

Parameter	Value
Bulk density (settled)	3.52 g/cc
Average agglomerate size	387 µm
Granule size (µm)	Fraction distribution
+ 350	61.7%
+212	13.4%
+150	6.4%
+90	10.5%
+53	5.5%
+38	1.5%
-38	1.0%

5.2.2.4 Applicability to the GPHS Product

The Granat process was designed to produce a mixed uranium-plutonium oxide. Its applicability to plutonium oxide, and specifically to Pu-238 oxide production, is unknown. However, for plutonium applications, the Granat method essentially simplifies to an enhanced plutonium hydroxide precipitation process using flocculation aids to ensure uniform, dense precipitates that can be dried and calcined without production of dust. So far, all of the testing of this specific process has been conducted in Russia. Testing with surrogates and ultimately with plutonium and Pu-238 would be required to optimize the process for producing Pu-238 GPHS and to quantify the purported advantage of the process – production of free-flowing, low-dust feed.

5.2.2.5 Granat Flocculation References

1. V. E. Morkovnikov et al, *Continuous Process of Powder Production for MOX Fuel Fabrication According to "GRANAT" Technology (Part 2)*, SSC RF VNIINM, 2000.

5.2.3 Resin-bead Loading and Calcination

5.2.3.1 Introduction

The resin bead loading and calcination process has been demonstrated with transuranics, including both curium[1] and Pu-238.[2,3] The process has also been used to produce fuel kernels for high-temperature gas-cooled reactor coated-particle fuel.[4,5] The process has two advantages that warrant its consideration, simplicity and generation of a dust-free product. Plutonium is loaded from nitrate solution onto ion exchange resin beads. The beads are then emptied from the column, dried, and calcined into PuO_2 beads, whose size are determined by the size of the precursor resin beads. Two types of resin loading are distinguished by the use of anionic or cationic exchange resin. Cationic exchange was successfully demonstrated with Pu-238 and is currently used for curium target fabrication, but anionic exchange was also determined to be potentially feasible for Pu-238 applications. Its use would seamlessly mesh with the current purification process.

5.2.3.2 Process Description

The process diagram for cationic exchange is shown in Figure 5-11. The plutonium nitrate feed stream arising from the precursor anion exchange purification undergoes a valence adjustment to ensure high-efficiency loading onto the resin. The nitrate is then fed into an exchange column containing cationic resin. Both the Pu-238 experience and current curium operations the process is based on use DOWEX 50W resin beads that have been previously sized and washed. However, other resins including nonsulfonated resins may prove more suitable for Pu-238 GPHS applications. A simple fractionation technique has been used to size the resin before introduction to the column, so that sizes of the final oxide beads can be controlled either as a mono-size or as a distribution within a controlled range. However, the resin is manufactured with a specific size range, which necessarily limits the variability in the final product.

After loading the plutonium onto the resin, the resin beads are emptied from the exchange column, dried, calcined, and subjected to oxygen exchange. Carbon residue from the resin itself can be removed through controlled oxidation during the calcination step. The oxygen exchange and granule seasoning operations should be possible in the same furnace. Figure 5-12 and Figure 5-13 show the equipment diagrams for the proven curium process this is based on.

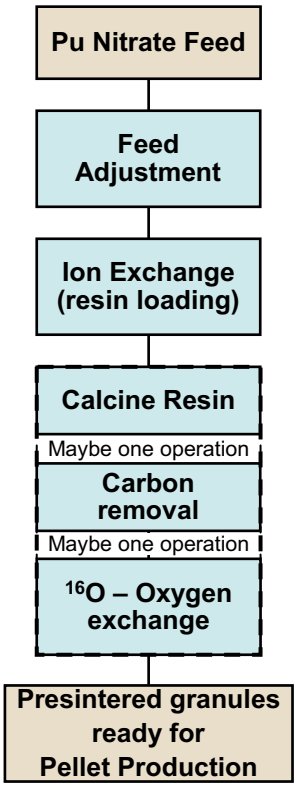

Figure 5-11. Oxide sphere production by resin bead loading and calcination.

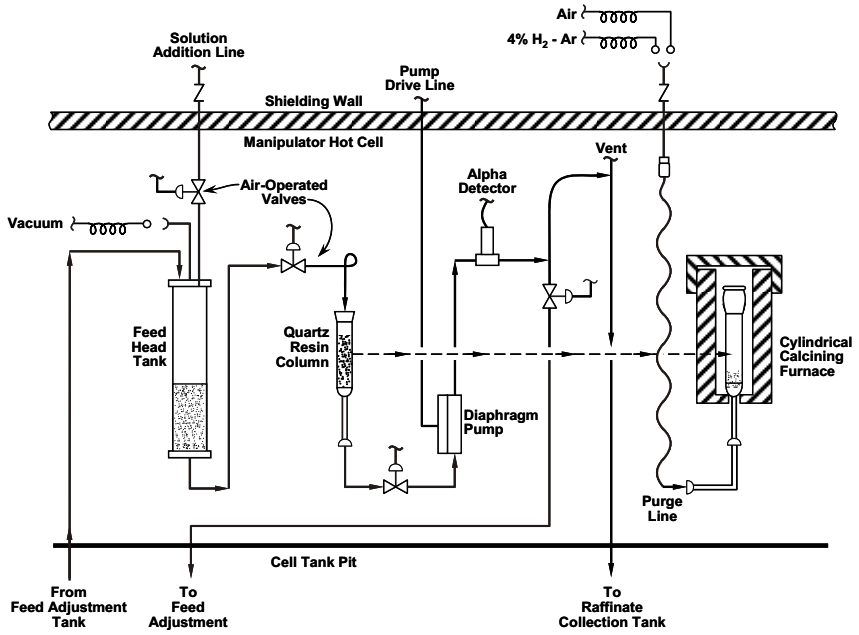

Figure 5-12. Diagram of hot cell resin sphere formation equipment.

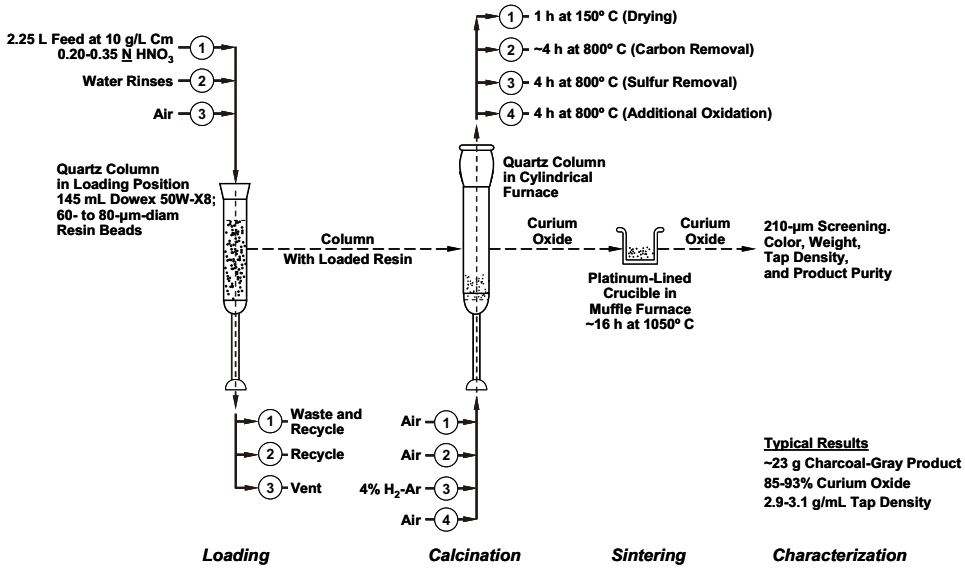

Figure 5-13. Column loading and resin calcination process.

5.2.3.3 Product Description

The current curium target process and the previous Pu-238 work include sintering at >1000°C, which produces dense, spherical particles with low ceramic activity. Based on conversion processes for sol-gel derived particles, carefully controlled drying and calcination at lower temperatures up to about 700°C should result in lower density spherical particles that retain internal porosity and ceramic activity. If successful, the two-part grog mixture used in the current reference pelletization process could be produced through appropriate control of the calcination and sintering conditions. The final oxide is essentially dustless; the only fine material results from particles either broken during handling or "popped" during calcination. The current curium product retains impurities originating in the resin at levels above those allowed in the Pu-238 GPHS. A key question for applying this process to Pu-238 GPHS production is whether a suitable resin and calcination/heat-treatment can be defined that achieves the desirable product purity while retaining adequate ceramic activity.

5.2.3.4 Process Characteristics

The ability to size the precursor resin beads allows control of the final oxide particle size, either as monomodal, bimodal, or continuous distributions as desired. The key concerns with the resin bead process for Pu-238 applications are selection of optimum resin, chemical impurities in the final product resulting from the resin itself, and retention of adequate ceramic activity in the oxide product.

5.2.3.5 Resin-bead Loading and Calcination References

1. F. R. Chattin et al, *Preparation of Curium-Americium Oxide Microspheres by Resin-Bead Loading*," New York, Oxford University Press, ACS Symposium Series, Vol. 161, 1981.
2. G. L. Silver, *Cation Exchange Method for Preparing 238-PuO_2 Microparticles,* MLM-1569, 1969.
3. G. L. Silver, O. R. Buzelli, *Loading of Sulfonic Acid Type Cation Exchange Resins With Tetravalent and Hexavalent 238-Pu*, MLM-1412, 1966.
4. Scott, J. L. et al., "Fabrication and Irradiation Behavior of Advanced Fuels for the HTGR," Carbon '72, 1972.
5. J. P. Drago, P. A. Haas, *Drying of Uranium-loaded Cation Exchange Resin with Microwave Heating*, ORNL/TM-5508, 1976.

5.2.4 Sol-gel Method

5.2.4.1 Introduction

"Sol-gel" refers to a group of related processes for producing microspheres. Sol-gel processes have been used extensively for producing nuclear fuel and target materials, including oxides, nitrides, and carbides of various actinides and actinide mixtures. A sol-gel process was also used early in the RPS program at Mound for fabricating DART and SNAP Pu-238 fuel forms.[1,2,3,4] The process was changed in the late 1960s from sol-gel to hydroxide cake precipitation and crushing to fabricate PuO_2 shards into molybdenum cermet fuel.[5] Among the variations, two classes are generally considered – internal and external gelation – the two differing principally in the source of ammonia used to gel a plutonium nitrate broth.

5.2.4.2 Process Description

The most directly applicable sol-gel experience, including all of the Pu-238 work conducted at Mound, used an external gelation process developed by ORNL.[6] However, for the current GPHS ceramic pellet production, internal gelation may prove to produce the better ceramic feed product. A generic flowsheet for an internal sol-gel process is shown in Figure 5-14.

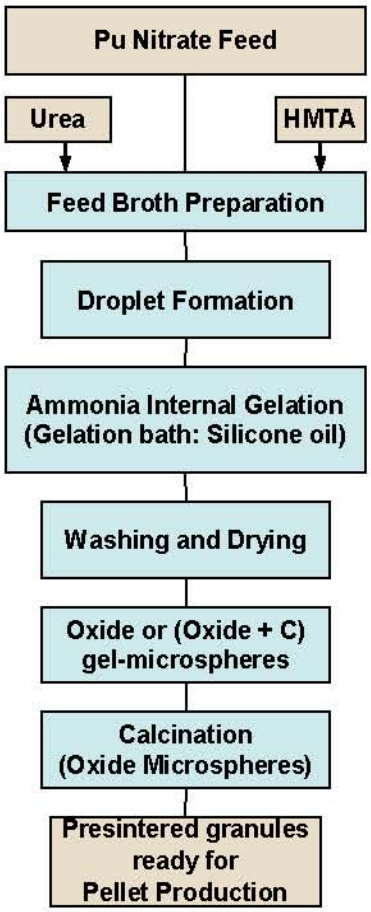

Figure 5-14. Process flow of internal sol-gel process.

5.2.4.3 Product Description

As shown in Figure 5-15, sol-gel products are typically uniform spheres that are essentially dust free. Because many of the applications of sol-gel derived microspheres require a fully dense, low-porosity product, drying and calcination conditions have often been optimized accordingly. Such products have essentially no ceramic activity. However, sol-gel derived microspheres have also been used to a limited extent for producing pellets.[7,8] For these applications, the drying and calcination temperatures are limited such that a fine-grained microstructure and internal porosity are maintained. The relatively soft and porous microspheres can be handled without damage, but break apart during pressing operations such that they lose their independent identities. Carbon, dispersed uniformly into the gel spheres, has been successfully used as a pore former during the drying/sintering step.

5.2.4.4 Process Characteristics

Sol-gel processes appear complex, but have been routinely used at pilot and production scale with actinides. In Mound's previous work with external gelation, the Pu-238's generation of internal heat was actually used as part of the drying process, and was determined to have no deleterious effect on the process or the product; however, pure plutonium oxide pellets, such as the GPHS, have not been fabricated from the sol-gel process. For GPHS applications, the key uncertainties relate to defining the optimum press-feed characteristics and adjusting the process to produce the desired product. Mixed-waste generation must also be considered and minimized; CCl_4 has typically been used to wash residual silicon oil from the green microspheres.

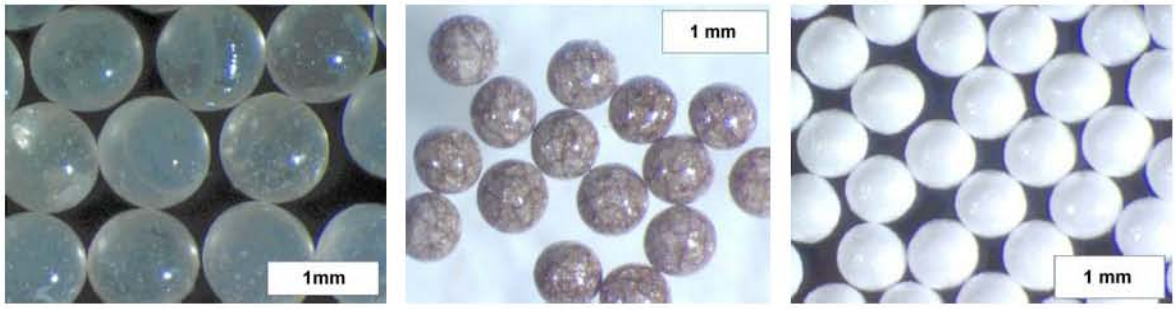

Figure 5-15. From left to right: Drip-casting microsphere formation of ZrO_2/Y_2O_3 spheres obtained by dropping Zr and Y nitrate solution into NH_4OH solution and drying; ZrO_2/Y_2O_3 spheres calcined 3 hours at 500°C; ZrO_2/Y_2O_3 spheres sintered 2 hours at 1600°C.[9]

5.2.4.5 Particle Size Adjustment References

1. Atomic Energy Commission, *Mound Laboratory Isotopic Power Fuels Programs: April-June, 1967*, MLM-1418, 1967.
2. D. L. Plymale, W. H. Smith, *The Preparation of 238-Pu Dioxide Microspheres by the Sol-Gel Process*, MLM-1450, 1967.
3. D. L. Plymale, *Exchange of Isotopically Enriched Oxygen With 238-PuO_2 Sol-Gel Microspheres*, MLM-1462, 1968.
4. Mound Laboratory, *Mound Laboratory Progress Report for Chemistry: October – December 1966*, MLM-1399, 1966.
5. PRHU Pellet Record, Mound Laboratory 1969, INL Mound Storage Container 165254.
6. R. G. Wymer, Laboratory and Engineering Studies of Sol-Gel Processes at Oak Ridge National Laboratory, ORNL/TM-2205, January, 200l, and P.A. Haas et al, *Sol-Gel Process Development and Microsphere Preparation*, ORNL-P-2159, Conf 660524-4, January 1966.
7. C. Ganguly, P. V. Hegde, "Sol-Gel microsphere pelletization process for fabrication of (U,Pu)O2, (U,Pu)C, and (U,Pu)N fuel pellets for the prototype fast breeder reactor in India," *Journal of Sol-Gel Science and Technology*, Vol. 9, 1977, pp. 285-294.
8. P. Naefe, E. Zimmer, "Sol-Gel microsphere pelletization process for fabrication of (U,Pu)O2, (U,Pu)C, and (U,Pu)N Fuel," *Nuclear Technology*, Vol. 42, No. 163, 1979.
9. P. G. Medvedev, private communication to S. M. Frank, Idaho National Laboratory, 2005.

5.2.5 Suspension/Temporary Binder Method

5.2.5.1 Introduction

As with the sol-gel method, plutonium oxide spheres are produced. The size of the oxide spheres can be controlled precisely and spheres can be produced from tens of microns to millimeter size. The difference with the suspension/temporary binder method is that the feed stream is an aqueous slurry of fine particle PuO_2 and organic binder. Droplets are produced that fall into a hardening solution. After that, spheres are then collected, dried, and sintered.

5.2.5.2 Process Description

Fine plutonium oxide powder (less than 20 μm) is mixed with an aqueous solution of sodium alginate to form homogeneous slurry. Alginate is the salt of alginic acid, an organic, unbranched binary copolymer that after cellulose is the most abundant biopolymer. The alginate binder is nontoxic and used worldwide in numerous processes for the pharmaceutical and food industries. The slurry is dispensed through an orifice, the size of which determines the dimension of the droplet. The orifice may be the tip of a syringe needle for manual production, or a vibrating single nozzle or multiple nozzles for automated production. The round droplets fall into a hardening solution of calcium chloride where the droplets harden into spheres. The spheres harden, owing to the ion exchange of Na alginate (water soluble) to Ca alginate that is insoluble in water. The metal oxide is not involved in the alginate ion exchange reaction. The spheres are cured in the solution, collected, and washed with alcohol to remove water and excess alginate and $CaCl_2$. As with the sol-gel process, washing is very important to maintain the integrity of the spheres and produce a pure product. Spheres are air dried at ~150°C to evaporate the wash fluid, calcined in air at ~550°C to fully decompose the organic binder. Actinide oxide spheres are then typically sintered in reducing conditions to form high-density spheres of PuO_2.

5.2.5.3 Product Description

This process produces PuO_2 spheres with precisely controlled size distributions. Microsphere diameter dimensions are determined primarily by the drop orifice diameter ranging from tenths of a millimeter to tens of millimeters. Typically, the microspheres are sintered at high temperature to produce high-density spheres of 96 to 99% TD, but conditions can be altered or pore formers added to decrease the sphere density with increased porosity. With sufficient sphere washing and calcining methods, impurities in the bulk spheres typically range from 10 to 500 ppm residual carbon and less than 150 ppm Ca and Cl.

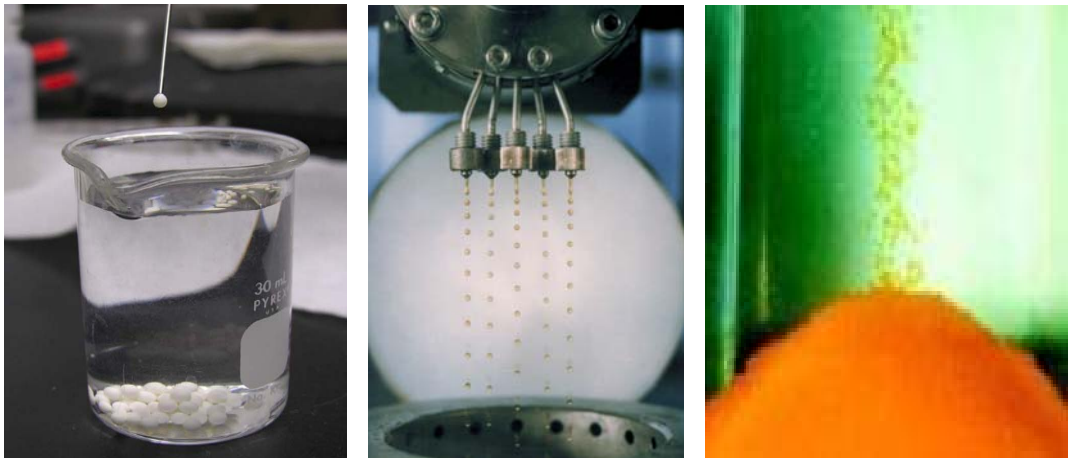

Figure 5-16. Manual drip-casting of CeO_2 slurry with binder into $CaCl_2$ hardening solution[1]; Automated drip-casting of UO_2 slurry (right-hand photograph).[2]

5.2.5.4 Process Characteristics

The suspension/temporary binder method requires a feed of fine PuO_2 powder of 20 µm or less. This somewhat defeats the dust-free requirements of the process. Once the PuO_2 powder is slurried with the binder solution, the process can be considered dust free as long as the powder remains wet. Once the spheres are produced in a well-controlled manner, very little fine powder is produced. The process can be performed either as a manual operation for small-scale sphere production or automated to produce kilogram quantities of spheres in a very short time. The process is simple, with minimal equipment or chemical requirements. With the exception of the Pu-238, the chemical reagents are nonhazardous. Some residue contaminates from the process remain in the product.

5.2.5.5 Suspension/Temporary Binder References

1. P. G. Medvedev, private communication to S. M. Frank, Idaho National Laboratory, 2005.
2. E. Brandau, *Microspheres of UO_2, ThO_2 and PuO_2 for the High Temperature Reactor*, BRACE GmbH, Taunusring 50, D-63755, Alzenau, Germany 2005.

5.2.6 Comparison of Alternate Conversion Methods

Table 5-5. Attribute comparison of granule formulation methods.

Attribute	Improved Oxalate precipitation	Granat Hydroxide precipitation	Sol-gel	Suspension/ Temp Binder	Resin	Modified Denitration
Fine powder production	Low	Moderate	Low	High – requires fine oxide powder feed slurry	Low	Moderate
Granule size distribution range	Moderate	Moderate	None-granule size specific	None-granule size specific	None-granule size specific	Moderate
Granule size control	Moderate	Moderate	Excellent	Excellent	Excellent	Moderate
Potential for introduction of impurities to product	Low	Low	High	Moderate	High	Moderate
Chemical reagent requirements	Low	Moderate	High	High	Low	Low
Process complexity	Moderate	Moderate	High	High	Low	Low
Desired product density	Excellent	Good	Poor	Poor	Poor	Good
Desired product porosity	Excellent	Good	Poor	Poor	Poor	Good
Desired product sinterability	Excellent	Good	Poor	Poor	Poor	Good

5.3 Alternate Pellet Production Methods

5.3.1 Improved Hot Press Pellet Production

In addition to the granule development work that SRS performed in the 1980s, SRS proposed an improved hot press pellet production.[1] Figure 5-17 contains an improved hot press flowsheet, presented by SRS with some of the process parameter details. This process is designed to have the granule process produce large, 40 to 100 µm agglomerates strong enough to hold together during subsequent processing, and yet still contain an agglomeration of small crystals (particles, 2 to 3 µm). In the current process, 40% of the agglomerates are heated to 1600ºC and 60% are heated to 1100ºC. In this improved process, 40% are also heated to 1600ºC, but the remaining 60% were heat treated while undergoing O-16 exchange during the granule production process and do not require any further heat treatment. The agglomerates are then reblended and loaded into the hot press die. Improved die materials or die coatings can reduce the interaction of the pellet with the die. Currently, about 6% of the pellet oxygen reacts with the graphite dies. This causes shrinkage during pressing. The reintroduction of O_2 is believed to be one of the primary contributors to cracking pellets.

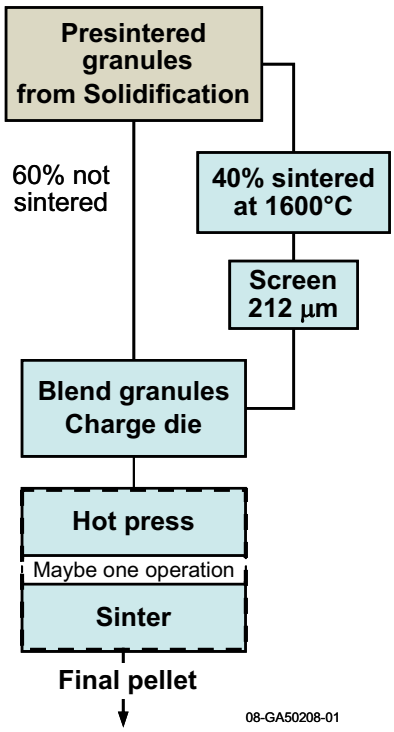

Figure 5-17. Process flow for improved hot press pellet production.

SRS reported that a total of eight full-size pellets were produced in an effort to develop and prove this improved approach. Unfortunately, only two pellets were made using the same parameters and the first of this set was dropped and broken during fabrication. Therefore, further testing is needed. During the test, fabrications die material, agglomerate heat treatments, temperatures, load pressures, and agglomerate blend mixtures were varied, so direct correlation to process parameters, PuO_2 feed properties, and final results cannot be quantified. The results, however, were encouraging and indicate that with proper control a consistent GPHS pellet could be manufactured with this approach. Pellets that met the density and grain size expectation of 82–85% TD and >10 µm respectively were made.

Successful SRS development of the direct fabrication approach focused on simplifying the steps needed to hot press the GPHS pellets. Advances over the past couple of decades in actinide ceramic material property information, measurement and computational techniques, and process behavior understanding may lead to developing a more sophisticated yet simpler approach to fabricating GPHS pellets than hot pressing. For example, the cold press and sinter process is simple but sophisticated, because judicious use of particle size, shape, impurities, surface activity, O/M level, temperature, and oxygen potential control density, shrinkage, grain size, etc., in PuO_2. The following alternatives consider these different technologies and their applicability to making GPHS pellets.

5.3.1.1 Improved Hot Press Pellet Production References

1. Glenn A. Burney, James W. Congdon, *Direct Fabrication of $^{238}PuO_2$ Fuel Forms*," DP-1621, July 1982, Savannah River Laboratory.

5.3.2 Liquid Phase Sintering of $^{238}PuO_2$

Direct sintering (pressureless) after cold pressing of as-calcined powder or milled powders has been studied by SRL, where researchers concluded that dimensions of the GPHS pellets were too difficult to control. Even when low temperature sintering achieved the goal of near 85% density, pellets continued to shrink at operating temperatures.[1] Sections 5.3.4 and 5.3.4.5 discuss preforming and pressureless sintering fabrication of pellets with improved dimensional control. In this section, pressureless sintering using a liquid phase is proposed as a method for fabricating dimensionally controlled pellets with controlled porosity. The liquid phase, it is contended, would allow presssureless direct bonding of high-temperature sintered granules (1600ºC) without using low-temperature, sintered, more active granules (1100ºC) in the standard GPHS pellet fabrication process. The low-temperature sintered granules don't appear to be necessary for the porosity of the microstructure. (See Appendix D1.) The liquid phase additive (1-5%) could be added as soft granules.

Two processing fundamentals are suggested. First, tighter dimensional control is easier if the total shrinkage is reduced by starting with a higher green density. This may be achieved by sizing the granules for optimum packing. (See Appendix D1.) Second, in the SRL study, pressureless sintering was stopped at the steep portion of the sintering curve,[1] making it difficult to both control dimensions and prevent further sintering in service. With liquid phase sintering it is possible to turn off the sintering at a prescribed density by drying up the liquid phase.

Possible liquid phase additives are $PuCl_3$-PuOCl (eutectic 747ºC) (see phase diagram in Appendix D1), PuF_3 (melting temperature: 1425ºC) and PuF_4 (melting temperature 1037ºC). To stop sintering after the liquid phase sintering has reached 85%, the chlorine in the oxy-chloride or fluorine in the liquid phase additive might be exchanged for oxygen by $H_2{}^{16}O$ treatment. In-process material may have higher than normal neutron emissions because of (α,n) reactions with the chlorine or fluorine. Neutron rates would return to normal after exchange with O-16.

Flow chart Figure 5-18 summarizes the process. All granules are high-temperature sintered at 1600ºC, then sized for a bimodal distribution centered at 20 μm and 140 μm by sieving. This achieves optimum packing (see Appendix D1). Granulated liquid phase additives are then mixed with the 1600ºC sintered granules and pellets are cold pressed. Pellets are then sintered at a temperature between 1400ºC and 1600ºC depending on the additive. Because of the uniform packing and high initial density, it should not be difficult to consistently achieve 85%. Finally, a postsinter treatment is performed to exchange O-16 and to reduce in-service shrinkage.

Liquid phase sintering would simplify the fabrication of GPHS pellets by avoiding hot pressing, and uses fewer soft, unsintered granules than direct sintering described in Section 5.3.4.5. However, it is an untried process for PuO_2 and would introduce chlorine or fluorine into the process stream. Furthermore, two conditions are necessary for liquid phase sintering—wetting of PuO_2 by the liquid phase and solution of PuO_2 in the liquid phase. It is likely that these two conditions would be satisfied at the high sintering temperature.

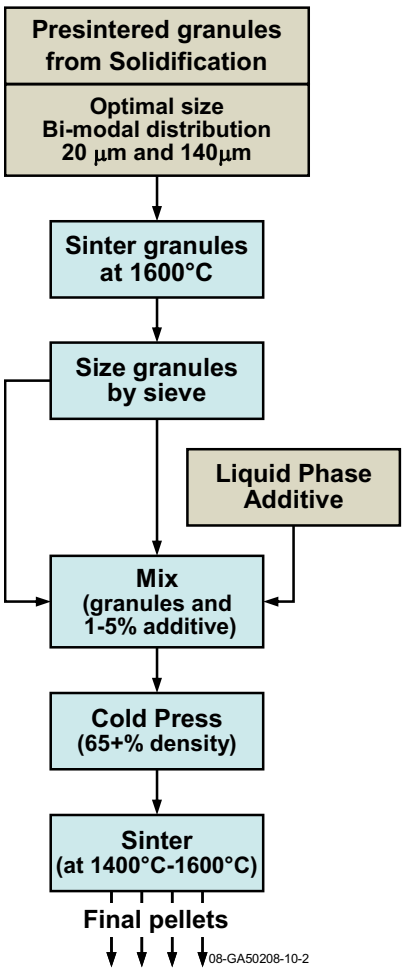

Figure 5-18. Process flow for pressureless sintering by liquid phase.

5.3.2.1 Liquid Phase Sintering References

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2. Kent, R. A., *LASL Fabrication Flowsheet for GPHS Fuel Pellets,* LA-7972-MS, 1979.
3. Lay, K. W.; Rosenbaum, H. S.; Davies, J. H.; Marlowe, M. O., United States Patent 4869866, 1989.
4. European Patent EPI482517.

5.3.3 Reaction Bonding of $^{238}PuO_2$

Reaction bonding is a well-known process for fabricating near net shape ceramic parts and can be adapted for processing of $^{238}PuO_2$ pellets. Reaction bonded aluminum oxide (RBAO) has been widely studied since the early 1990's,[1,2,3,4] and because of similarities between the two systems it can act as a reference from which reaction bonded PuO_2 (RBPO) can be developed. (See Appendix D2.)

In the reaction bonding process, metal powder (30-80%) is mixed with oxide powder and then cold pressed into a desired shape. The pressed part is subjected to a controlled P_{O_2} atmosphere at a controlled heating rate to oxidize the metal. Upon oxidation, the metal expands, filling into the pores and bonding strongly with the oxide powder. For instance, Al expands 28% when converted to Al_2O_3. Initial oxidation rigidizes the skeleton of the part so near zero further expansion or contraction of the part occurs. (See Appendix D2.)The advantages of the process as demonstrated by RBAO are:

- Near net shape. (See Appendix D2.)
- Because the metal powder is ductile, it acts like a binder for pressing, giving it a high green strength. In fact, binderless, cold pressed parts can be green machined.[2]
- Reaction-bonded ceramics have a high strength. Some results indicate better strength than sintered Al_2O_3 of comparable porosity.[2] (See Appendix D2.)
- High permeability to gases. RBAO has been used as permeable catalyst support because of excellent gas permeability.

In the RBAO process, fine Al powders are passivated, so handling and pyrophoric reactions are not a problem. Nevertheless, the risk of introducing fine plutonium metal into a glovebox with the off chance of undergoing a rapid pyrophoric reaction is too great. Thus, the process must be altered. It is proposed that the starting point would be granules sintered at 1600ºC as shown in the flow chart, Figure 5-19. In this process it is particularly important to start with a high green density, because the final density is directly determined by the green density (see Appendix D2), so again, bimodal distribution is used. The proposed next step is to reduce the powder surface PuO_2 to a sub-oxide (e.g., Pu_2O_3), by introducing the granules into an H_2

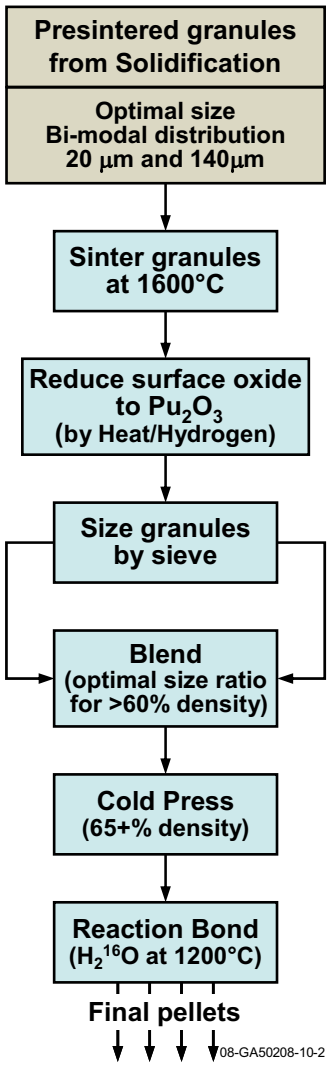

Figure 5-19. Process flow for fabrication of GPHS pellets by reaction bonding.

atmosphere at approximately 1000ºC for a short time (to be determined). This step substitutes for mixing in fine metallic powder. The sub-oxide, being denser than PuO_2, is subsequently reoxidized to PuO_2 and expands to fill the pores. This would be the reaction bonding step. The thickness of the sub-oxide surface is dictated by how much is needed to expand into the pore for 85% density in the final part. In Appendix D2, it is estimated that the thickness on a 50 μm diameter granule need be only 1.4 μm.

Although the reaction bonding process should be favorable for this application because it is so simple, questions remain. In the RBAO process, Al powder fills the interstices between the Al_2O_3 granules. During the reaction bonding process, the Al oxidizes and expands to more fully fill the interstices. In the proposed RBPO process, a sub-oxide forms on the surface. Upon oxidation, if it merely expands back without filling the pore and strongly bonding the granules, the process would be unsuccessful. If, however, during formation of the Pu_2O_3 in the H_2 atmosphere, the sub-oxide is broken into a powdery coating and during pressing is forced into the interstices, the process will be successful.

Another potential problem is self heating of $^{238}PuO_2$. In the RBAO process, careful temperature control is required to avoid "run away" caused by the exothermic nature of the oxidation reaction. Fortunately, the control can be mitigated by oxygen demand ($H_2{}^{16}O$) furnaces, which are commercially available and can be used to control the reaction rate.

This proposed reaction bonding process is perhaps the simplest of the processes and least likely to generate fine particles, if it works properly. It would also lead to a higher strength pellet, but it would require a development effort. There is some risk it would not work because the proposed process is quite different than the RBAO process.

5.3.3.1 Reaction Bonding References

1. S. Wu, D. D. Holz, N. Claussen, "Mechanisms and kinetics of reaction-bonded aluminum oxide ceramics," *Journal of the American Ceramic Society*, Vol. 76, No. 4, 1993, pp. 970-980.
2. E. Suvaci, G. Simkovich, G. L. Messing, "Reaction-bonded aluminum oxide Process I, the effect of attrition milling on the solid-state oxidation of aluminum powder," *Journal of the American Ceramic Society*, Vol. 83, No. 2, 2000, pp. 299-305.
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4. S. Bertrand et al, "Processing, microstructure and mechanical strength of reaction-bonded Al_2O_3 ceramics," *Ceramics International*, Vol. 29, No. 7, 2003, pp. 735-744.
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5.3.4 Preforming and Sintering Techniques

5.3.4.1 Introduction

Hot pressing of presintered granules to produce a densified PuO_2 pellet can be replaced by preforming (e.g., green pressing) followed by solid state (pressureless) sintering. The motivation to replace hot pressing by preforming (green pressing) of pellets followed by pressureless sintering is to: (a) reduce cracking in the final pellet owing to surface reduction and reoxidation that happens in the current hot pressing process, (b) produce more homogeneous and controllable pellet microstructures, (c) greatly reduce production costs by eliminating the expensive, high-strength, machined-to-high tolerance graphite dies (one-use consumption), and (d) reduce production costs and speed up production (reduce radiation exposure rates) by using rapid green pressing methods followed by densification of many parts concurrently in a single furnace run.

In general practice, pressureless sintering requires using fine crystallites with large surface areas to drive the densification. However, fine granules are not always needed to result in sufficient densification. In addition, if some fine granules are needed, potential exposure to respirable fines of PuO_2 can be dramatically reduced by using special granulation methods, and through improvements to material handling and containment (see Section 5.5).

The current method of hot pressing of PuO_2 at high temperatures is most likely a combination of hot forging, where the hot PuO_2 cubic-crystals are plastically deformed owing to dislocation motion (glide/climb),[1] and/or pressure-aided sintering, where the reduction of surface area driving force for atomic diffusion[2] is added to by a linear pressure term. Therefore, hot pressing can accept feed granules with reduced surface area (activity) when compared to pressureless sintering.

5.3.4.2 Preforming (Green Pressing)

The pressing (cold/green or hot) of ceramic pellets of the GPHS geometry in an ordinary metal or graphite die leads to stress/density variations as detailed in Appendix D3. These stress and density variations lead to dimensional variations and cracking in the final sintered part. The best way to avoid these problems is by using the preforming technique of isostatic pressing shown in Figure 5-20. A cylinder resulting from this technique is illustrated in Figure 5-21. The most applicable isostatic pressing method for use in a glovebox atmosphere is Dry-Bag Isostatic Pressing. This is shown schematically in Figure 5-22 for the commercial production of a ceramic spark plug insulator.

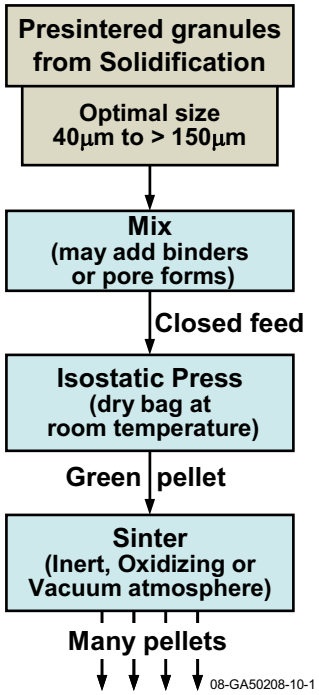

Figure 5-20. Process flow for isostatic pressing.

5.3.4.3 Granulation, Packing, and the Use of Green-forming Aids (Additives)

Binders and lubricants are frequently used in green pressing. Problems associated with their use in preforming $^{238}PuO_2$ derive from the radiation and heat generated by $^{238}PuO_2$ that over time will tend to damage or destroy the function of most organic additives.

A number of ceramic materials are green-pressed (or otherwise formed) without using organic additives. If the shape of ceramic crystallites and granules are controlled, they can be pressed to provide sufficient interlocking and binding forces. Then additives are not needed. Ceramic pellets containing AmO_2 have recently been produced by the French without using any binders.[3] No organic binder was used owing to radiation damage from the AmO_2. However, a special three -piece metal die was designed and built to uniaxially press pellets (double-acting press) as shown in Appendix D3.

Using traditional organic binders and lubricants would be severely limited for green-forming $^{238}PuO_2$ powders or granules, owing to internally generated radiation and heat. (See Appendix D3.) As noted in Appendix D3, the possibility exists for using organic binders/pore formers that convert into “char” when they are heated in an inert atmosphere and therefore retain mechanical strength and adhesion. Later, these binders can be burned out as part of sintering in an oxygen-containing atmosphere. These binders are named in Appendix D3. Using these binders can also be useful in creating large residual pores in ceramics.

It also seems possible to develop “sticky” inorganic binders resistant to heat and radiation that “set” (like a cement) when heated. Examples of these materials are in Appendix D3.

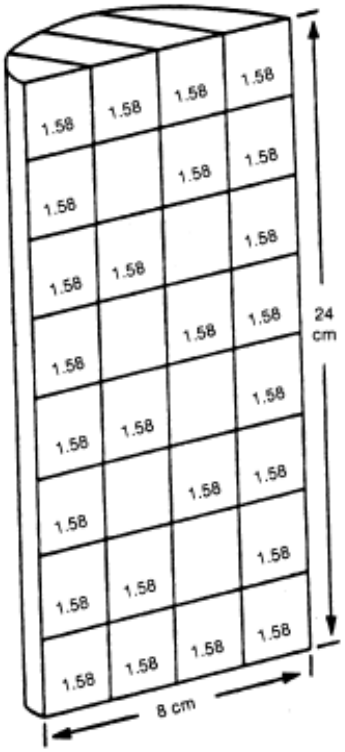

Figure 5-21. Uniform density is achieved in a solid cylinder by isostatic pressing.[4]

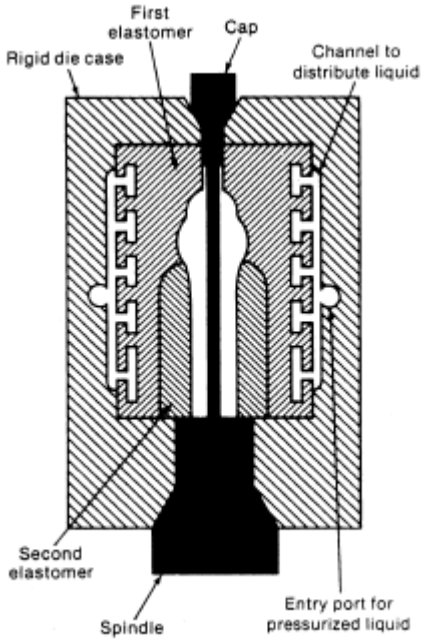

Figure 5-22. Schematic of a die for dry-bag isostatic pressing of a spark plug insulator.[4]

Historically, solid state sintering has utilized powders with fine, active particles (crystallites) with median diameters in about the 0.3 μm to 3 μm range. However, using fine particles (derived from ball-milling) of $^{238}PuO_2$ has caused glovebox contamination problems. This is especially true for the manual "slugging" and screening process used to produce green granules (Appendix D3).

To reduce glovebox contamination from fine powders, it will be necessary to replace the slugging method with other methods to produce granules (soft/lightly bonded crystallites, or hard/highly bonded crystallites). Alternate methods to produce different types of granules are covered in Sections 5.1 and 5.2. Appendix D3 also explains how selecting proper weight fractions for mixing of various granule sizes can lead to optimized packing (high green density). This approach is illustrated in Figure 5-23 for two sizes (coarse and fine) of spherical particles where the maximum packing fraction is achieved when the ratio between nearest sizes is greater than about 7 and the finer particles are dispersed in interstices.

When using sintered (hard) granules, it is important to select granule sizes so that they pack to a high tap density. These granules could then be green-pressed (e.g., dry-bag isostatic press) to achieve even higher green density. A practical value for these green densities might be in the 70% TD range. When pressed, adjacent sintered granules will touch, so that there will not be much shrinkage during sintering (e.g., to 82-86% TD). This process ensures better dimensional tolerances on the final sintered part.

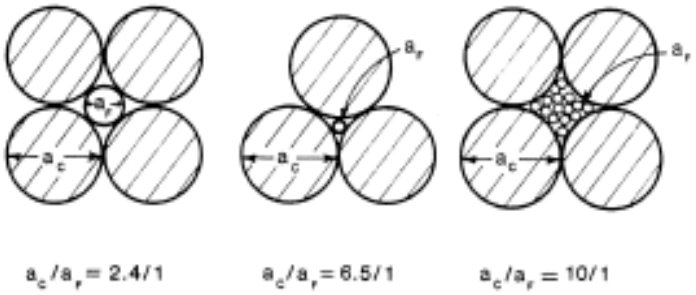

Figure 5-23. Packing of fine spheres in a planar interstice among coarse particles: a_c = diameter of coarse particle, a_f = diameter of fine particle.[5]

From a hazards point of view, it would be desirable to minimize or completely eliminate the respirable fines from the sintering process and still achieve the desired density and some strength. This can be achieved in two ways:

1. The formation and use of soft agglomerates consisting of fine, active, particles with the addition of binder/pore formers that minimize airborne respirable fines (as previously discussed).
2. Using sintering techniques that don't require fine particles.

An example of a very soft agglomerate is shown in Figure 5-24 (A). This as-received zirconia granule can be easily ground or dispersed into small aggregates of very fine crystallites (Figure 5-24 (B)). These very soft agglomerates also deform easily under pressure to homogeneously fill space during green pressing. The drawback is that very soft agglomerates can shed some small crystals during handling and would need to be enclosed/contained as much as possible. A somewhat tougher soft granule can be formed by spray granulation or spray drying where a binder is added. Or a soft agglomerate can be made stronger by a heat treatment that lightly sinters the individual crystallites together to form "necks." Figure 5-25 shows an example of spray granulation. Spray granulation is the formation of granules when a liquid or a binder solution is sprayed into a continually agitated powder. As discussed in Appendix D3, a radiation-resistant organic binder or inorganic binder could be used for granulating $^{238}PuO_2$ crystallites and also serve as a residual pore former. An example of "very tough" granules formed by spray-drying, followed by a low-temperature sintering is shown in Figure 5-26.

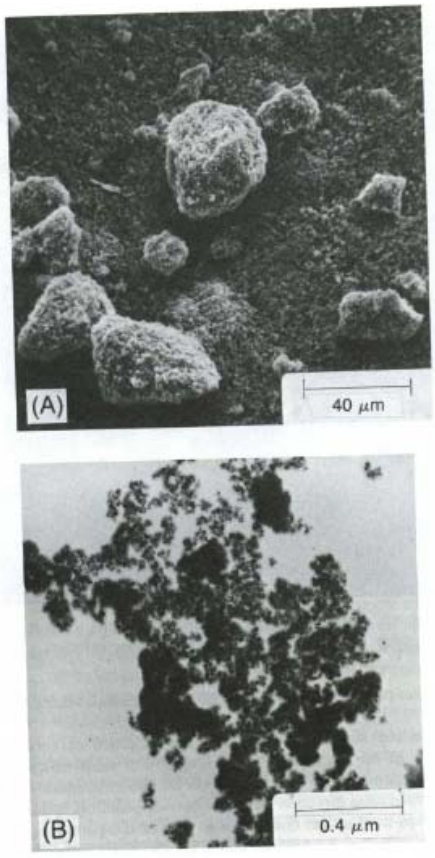

Figure 5-24. Very soft agglomerates/granules (A) are easily dispersed into small aggregates of very small crystallites (B).[5]

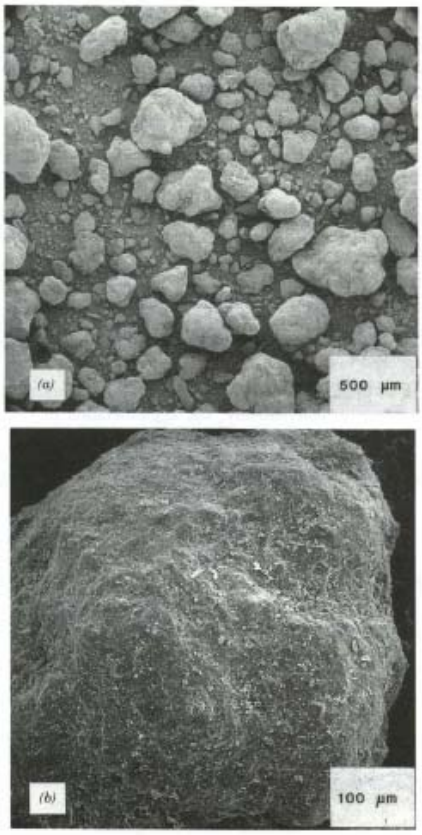

Figure 5-25. SEM micrographs of soft granules strengthened by use of a binder. Formed by spray granulation (a) general view and (b) shape and surface smoothed by rubbing during tumbling.[5]

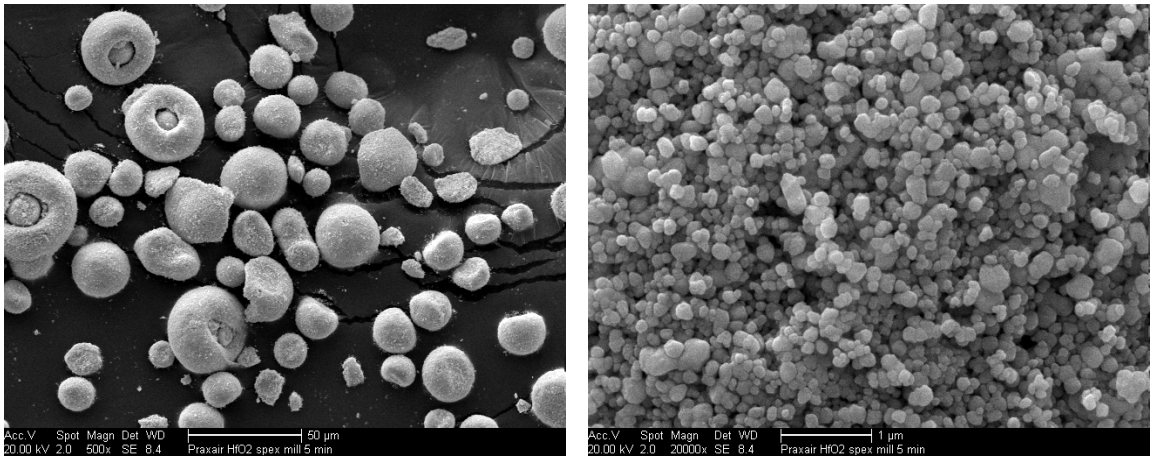

Figure 5-26. SEM micrograph of very tough granules of spray-dried and lightly sintered HfO_2 powder. Rounded granules (left) consisting of neck-bonded crystallites (right).

5.3.4.4 Preforming Techniques References

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5.3.4.5 Pressureless Sintering of $^{238}PuO_2$

To achieve high final densities (e.g., 85-90% of TD), pressureless sintering requires a more active input feed of either fine crystallites or soft granules for green pressing than for hot pressing. The fine crystallites (if not agglomerated) will have a low fill density in the die and therefore result in a high compaction ratio. This can lead to variations in the final sintered dimensions. Soft granules can uniformly fill the die and are deformed under pressure to produce a uniform density. Therefore, the compaction ratio is reduced and final dimension variations are reduced. Stronger, tough granules do not deform well under pressure and require a graded-size packing approach (see Appendix D3) to achieve good green and final sintered densities.

Sintering of pellets made using a graded-size packing approach is shown in Figure 5-27. Two types of granules were mixed and the agglomeration conditions, additives, and pressure were varied between the two samples. The sintering schedule was fixed (i.e., a high sintering temperature). These pellets exhibit the approximate percent of theoretical density (82-87% TD) that is required of $^{238}PuO_2$ GPHS pellets. If larger pores are desired in the microstructure, then pore formers can be used as described in Appendix D3.

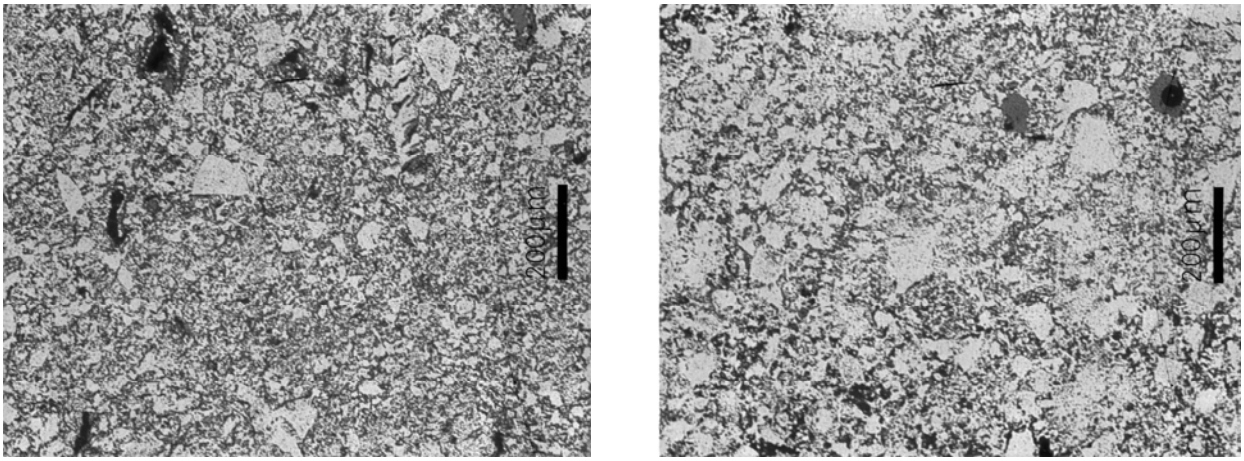

Figure 5-27. Examples of samples sintered with mixture of sizes of hard granules. Left: 87% TD (100X) Right: 82% TD (100X).

5.3.5 Spark Plasma Sintering of $^{238}PuO_2$

If hard, dense granules are desired as a feedstock, then pressureless sintering will not produce sufficient final density. For optimally-packed, hard, prefired granules, the density likely could be increased to the 82-86% density range by using the new spark plasma sintering (SPS) technique (field activated sintering) shown in Figure 5-28. This technique, illustrated in Figure 5-29, is currently being studied.[1,2,3] It is suggested that contact areas between hard granules would be activated and bonded.

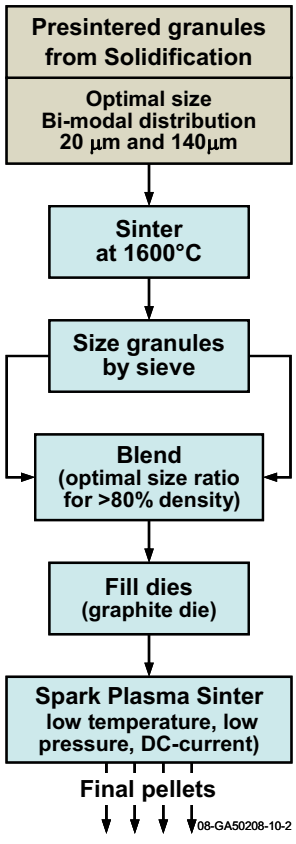

Figure 5-28. Process flow for spark plasma sintering.

In the SPS process, powders are loaded into a graphite die and heated by passing an ON-OFF DC pulse through the assembly.[4] Therefore, this method could be considered a low-pressure, lowered temperature, electrically activated, hot-pressing method. This activation can be generated by: (1) spark plasma, (2) spark impact pressure, (3) Joule heating, and (4) an electrical field diffusion effect. The actual mechanisms dominating for specific ceramic (low-electrical conductors) powders are unclear; however, enhanced sintering at lower temperatures and enhanced reactivity of powders have been noted.[5] This includes nonelectrically conductive ceramic powders like zirconia[6] and ceria (with resulting grain sizes approaching 10 nm), and alumina.[7] The alumina was fully densified at much lower temperature (1150°C) within a much shorter time (minutes), than in conventional sintering processes. It was suggested that densification was enhanced in the initial part of the sintering cycle by local spark-discharge process in the vicinity of the contacting particles, and that both grain-boundary diffusion and grain-boundary migration were enhanced by the electrical field originating from the pulsed direct current used for heating the sample. Commercial furnace units are available[8] and multiple pellets can be pressed during one run. Low pressure is used; generally only enough to maintain good electrical contact between the platens and the powder or the graphite die.

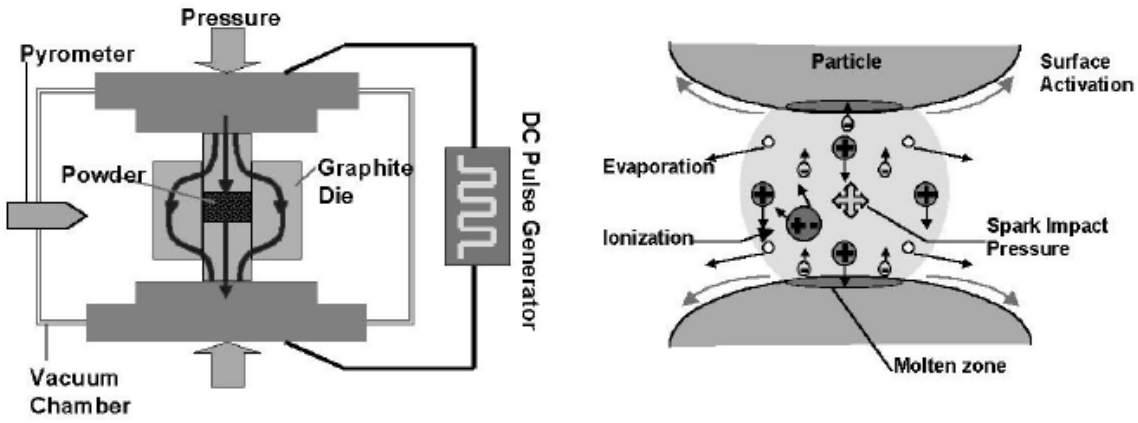

Figure 5-29. Schematic and spark plasma sintering and accompanying activation effects.[4]

5.3.5.1 Spark Plasma Sintering References

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5.3.6 Superplastic Forming of $^{238}PuO_2$

Superplastic forming is another process that eliminates stream handling of fine powder, and has good dimensional control. The term superplasticity refers to materials that can achieve abnormally high ductility. For instance, ceramics that can deform to greater than 100% strain under tension at a high temperature are termed superplastic.[1] The term superplastic forming usually describes forming of a fully dense piece of fine-grained material into a particular shape by some pressure-forming operation, such as deep drawing. However, here it is used to designate ductile deformation of granules. If a fine-enough grain size can be maintained in most of the granules, the granules will deform superplastically in a hot press, densifying by filling in the voids much like a pressed ductile metal. The grain size in superplastic ceramics needs to be on the order of 1 μm or less.

To maintain sufficiently fine grains in dense granules, it may be necessary to sinter them by SPS at a low temperature. After the granules are sintered to near full density, they are mixed with the 1600ºC sintered grained granules (using high pressures) and hot pressed to the desired final density. (See the flow chart in Figure 5-30.)

Figure 5-31 shows a microstructure in its early stages of superplastic forming in which the granules have bonded via diffusion.[2] It is shown in Appendix D4, from a study of hot pressing of Y_2O_3 stabilized ZrO_2 superplastic granules, that the densification rate is independent of granule size, and depends only on the grain size. Appendix D4 also shows that a very favorably microstructure may be obtained.

This process has the advantage that no-low temperature sintered granules (1100ºC), are needed. Therefore, the postpress pressureless sintering will result in no additional shrinkage. Also, only well-sintered granules will be introduced into the hot pressing die. The primary risk in adopting the process would be that sufficiently fine-grained granules could not be obtained.

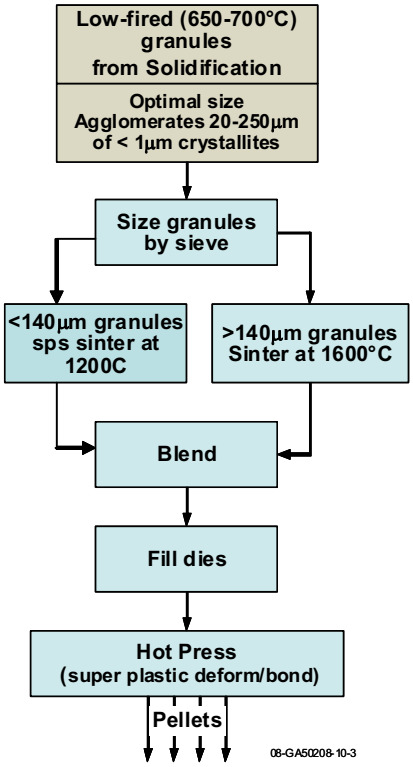

Figure 5-30. Process flow for the superplastic forming process.

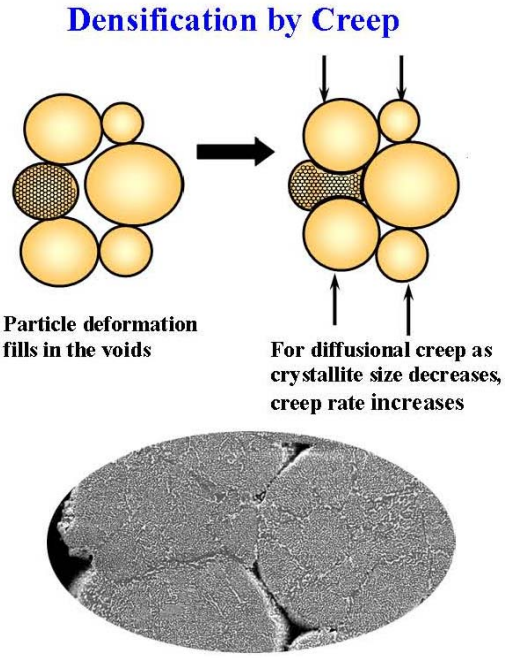

Figure 5-31. Superplastic deformation of nanocrystalline granules.

5.3.6.1 Superplastic Forming References

1. I. W. Chen, L. A. Xue, "Development of superplastic structural ceramics," *Journal of the American Ceramic Society*, Vol. 73, No. 9, 1990, pp. 2585-2609.
2. H. Keshavan, *Forging of Melt Quenched Powders: Microstructure Development and Kinetics of Densification,* Rutgers University, Ph.D. thesis, 2006.

5.4 Alternate Fuel Forms

Some alternate GPHS fuel forms were briefly examined, looking for possible advantages such as ease of manufacture and enhanced performance compared to the current oxide ceramic pellet form. A large testing data base, based on the current oxide pellet form, supports the safety envelope in the Final Safety Analysis Report for RTGs. A significant advantage would need to be demonstrated to change to a new form or design, to justify the amount of development, testing, and flight-ready testing.

The basic requirements that all fuel forms will have to meet include the following:

- Sufficient heat loading to meet mission requirements, >4.0 watts/cc
- Sufficient open porosity to allow helium to escape over the operating lifetime, <88% TD
- Sufficient strength and integrity to hold together during launch and operation, and enough strength to meet impact test requirement
- Compatibility with cladding material and cladding vent.

None of the fuel forms involving final particles from sol gel, or coated particle fuels, cermets, cercers, etc. passed the initial consideration because they could not meet one of more of the criteria. For example, they all failed the watts/cc requirement because of dilution with the matrix material and the open porosity (low density) requirement.

Two other ceramic forms of Pu were considered, PuN and PuC. Both have advantages over their oxide counterpart because of high thermal conductivity (~10 times that of oxide) and increased Pu loading. But PuN is not worth developing because of the alpha-neutron reaction with both N-14 and N-15. Nitrogen may escape in an open system during normal operations and potential temperature excursions. PuC, on the other hand, may be an acceptable fuel form because there are no reported alpha-neutron reactions and a pellet will operate at lower centerline temperature because of the high heat conductance. One disadvantage may be the addition of a carbothermic reduction step in the process.

No known plutonium metal alloys or elemental compound phases have both high melting points (>1200˚C) and high enough Pu density to meet the watts/cc and open porosity requirements for GPHS units. Silicon is the only element that forms phases with Pu that melt above 1200˚C and have 60% or greater Pu content. See Table 5-6.

Table 5-6. Alternate fuel materials.

Pu-element Phase	Atom % Pu	Melting Point (˚C)	Pu-238 Density (g/cc)	Heat Rate (watts/cc)
Pu_3Si_2	60	1440	7.336	4.1
PuRh	50	1260	6.956	3.9
PuPt	50	1250	6.111	3.4
PuSc (solid solution)	50	1200	6.115	3.5

Pu_3Si_2 produced at 85% TD would have a high melting point of 1440°C and would produce an acceptable amount of energy at 4.1 watts/cc.

5.4.1 Alternate Fuel Forms References

1. Alpha-neutron Reaction Calculator, www.wise-uranium.org/ranc.html.
2. F. A. Ellinger et al, *Constitution of Plutonium Alloys*, LA-3870, January 1968.

5.5 Baseline with Material Handling Improvements

During review of the current process and alternate concepts, numerous systems were identified that could be implemented to improve production. These systems hold as much promise in improving the current process as being implemented with alternate processes. These systems have the potential of improving quality and preventing contamination spread. This section discusses areas of potential improvement and the systems that warrant further consideration. The areas of improvement include material handling, particle size reduction, and powder characterization.

All operations requiring the handling of unencapsulated $^{238}PuO_2$ are performed in gloveboxes that are constructed with stainless steel lead-stainless steel sandwich-type walls and highly polished walls to facilitate cleaning. Glovebox windows are safety glass held in position by viton gaskets with stainless steel fire shields. The gloves consist of two layers of Hypalon® separated by a thin layer of lead. Four inches of hydrogenous shielding (Lucite panels over glovebox windows and water-filled tanks elsewhere) are located outside the glovebox and provide neutron attenuation.[1]

The process gloveboxes are provided with either argon or helium atmospheres. Gloveboxes are attached to one another via vacuum/inert-gas airlocks for protecting neighboring gloveboxes if one glovebox is breached.[1]

Current operations include manual or hands-on processing using shielded gloves to handle the material directly within the glovebox. The production of encapsulated GPHS pellets from plutonium-oxide powder was presented in Section 2.3.

5.5.1 Lessons Learned by LANL GPHS Production

During the pellet production phase of the Cassini Project, various problems and challenges occurred, including equipment failure and containment breaches. A furnace core tube, heating element, and thermocouple replacements shut down operations for several days.[2]

Once the material was moved into the glovebox system, the fuel was sampled for impurities using a grab method. Owing to the lag time between sample acquisition and laboratory results, the material exhibiting unacceptable impurity levels had progressed through the granule seasoning stage and had to be scrapped after several days of processing. In a later attempt to speed production because of potential analysis failure, 25 lots were stored in line after O-16 exchange until analytical results were reported. The increased volume of material stored throughout the processing area increased background levels, raising worker exposure levels. Materials having unacceptable impurity levels were either scrapped outright or before more extensive processing, and new blends were created resulting in pellets with acceptable purity levels.[2]

Window seal gaskets in two gloveboxes were badly decomposed and required change out. A window change glove bag contamination containment system was mandated. During three window changes, the containment bag system developed leaks to the room, requiring decontamination efforts. Another stand down occurred the following year because maintenance activities produced holes in the containment bag seals, thereby contaminating the room again.[2]

Conclusions included that the homogenization step (milling) should occur before obtaining initial fuel samples, therefore increasing the chances that sample results would be replicated and that analysis turnaround should be faster.[2]

Typical problems with the current process include low throughput caused by equipment and containment failures.[2] Product loss occurred because of containment breaches, which also increased worker exposure. Decontamination efforts were time consuming, labor intensive, and costly because the product migrated throughout the entire room.

Improvements may include highly contained processing with an enclosed and automated system within the gloveboxes. High-containment components (i.e., high-containment valves, double-sealed ports, pneumatic conveying, vacuum dust collection) are available for material processing within the glovebox system, which could decrease cleanup and decontamination efforts, reducing worker exposure and waste generation. A vacuum dust collection system would reduce product loss by allowing dust emission collection at dynamic seals and openings, and recycling the material back to the system for processing. An online sampling and analysis system would provide immediate data on the enclosed system, which could significantly increase throughput. A more automated system could remove the operator from close proximity to the process, which would further reduce worker exposure.

5.5.2 Powder Technologies Reviewed

Technologies were reviewed and evaluated for potential improvement. Technologies listed under the following general areas were considered (refer to Appendix F for details of individual technologies):

Material Handing

- Highly enclosed processing
- Gravity flow
- Pneumatic conveying
- Screw conveyors, mixers, and feeders
- Vacuum dust collection
- Magnetic-coupled drives and components
- Cleanout devices and techniques

Particle Size Reduction

- Ball milling
- Attrition milling
- Granulation

Powder Characterization

- Digital image processing
- Laser spectrometry
- Porosity/differential pressure.

5.5.3 Discussion/Evaluation

Highly contained processing includes containment valves that provide minimal risk to product contamination or worker exposure because of metal-to-metal seal, intermediate chamber, and a vacuum plug. The valves are effective to nanogram levels of containment. Other high-containment items are double-sealed ports and liners.

Other material handling techniques include gravity flow and pneumatic conveying. Material holdup may present challenges in gravity flow systems. Glass tubing and other components may be used to view material movement. Pneumatic conveying can be a closed system to minimize product loss.

Screw conveyors, mixers, and feeders are versatile and could be sealed from the glovebox interior atmosphere. Dust vacuum nozzles may be placed in the process at points susceptible to dust emissions and the vacuumed material may be reintroduced to the process for recycle and reuse. Magnetic-coupled drives and components may be used for the benefit of highly enclosed and sealed processing. Special system cleanout devices may reduce worker exposure, aid in maintenance activities, and reduce process down time.

Particle size reduction methods include planetary ball mills, mixer ball mills with or without cryogenics, and attrition mills.

Planetary ball mills are capable of reducing the particle size to 0.1 μm and rotate around vertical axis for use in a gravity feed system. Other potential benefits of planetary ball mills include: (1) a large material selection currently exists from the vendor to replicate the existing system, (2) parameter versatility, (3) can operate in dry or wet systems, and (4) is a fast particle size-reduction technique. Disadvantages may be that the ball mill is hard to clean, worker exposure may increase because of additional handling, and impurities are introduced from the ball and housing components.

Mixer mills are capable of reducing the particle size to 10 μm and may be used with cryogenics to reduce grinding time. Mixer mills rotate on the horizontal axis and, therefore, would not work as well with a gravity feed system, although this issue could be addressed through automation. Mixer mills may also be hard to clean.

Attrition mills are versatile because variables such as grinding media size, type, and amount, machine speeds, and feed rates can be modified. Other advantages of dry grinding attrition mills are low power consumption, low maintenance, compact design, easy and safe operation, and machine tanks may be jacketed for cooling. Some limitations of attrition mills are: feed material sizes are limited for most submicron superfine powders, wet grinding may be necessary, dry grinding generates more internal heat than wet grinding, and availability of parts may be limited.

Granulation may be accomplished by either a dry or wet process. Fine powders can be processed into densified sheets by using mechanical pressure exerted on two compacting rolls, which then can be granulated to any desired mesh size. Fines may be minimized by including a screener and recycle system that provides control of the final particle size and density. Wet granulation requires that a liquid solution be rapidly dried over an active ingredient. A suitable liquid solution was not identified during this evaluation and therefore wet granulation is not viewed as a viable option.

Material characterization may be provided by digital image processing or laser spectrometry to determine particle size or shape. Digital image processing uses computer algorithms to perform image processing on digital images, allowing a much wider range of algorithms to be applied to the input data and helping to avoid problems such as noise build-up and signal distortion during processing. Image analysis can be used to measure particle sizes from 0.5 μm to 2 mm. Image analysis captures a two-dimensional image of the three-dimensional particle and calculates the particle size and shape. The digital imaging processor software is user friendly, plots trends between multiple records, compares multiple results, compares and clusters data, and provides reports.

Laser spectrometry can provide particle size data as low as 0.1 μm and may be either an automatic continuous online operation or manual at-line. Software interfaces with other process control systems and can operate with hazardous substances.

Porosity may be determined online using a device that measures either air permeability or air resistance.

5.5.4 Baseline with Improvements References

1. Kent, R. A., *LASL Fabrication Flowsheet for GPHS Fuel Pellets*, University of California, August 1979, pp. 9-28.
2. McCormick, Egan D., *The Cassini Project: Lessons Learned through Operations*, LANL, LA-UR-97-3242, 1997, pp. 1-5.

5.5.5 Summary/Recommendations

Many options are available regarding highly contained material-handling equipment to enclose the process and can vary from a manual operation to highly automated.

Attrition mills appear to be the best choice for the particle size reduction because of their versatility. Research shows that planetary ball mills may provide slightly lower particle sizes than attrition mills, but may be more difficult to implement in a continuous operation with workers handling the material more often. The dry granulation process may be enclosed, with flexibility of the particle size, and is preferred to the wet granulation process. Laser spectrometry can provide information regarding particle size but not particle shape as with the digital imaging analyzer. The particle size determination is slightly more limited with the digital imaging analyzer (as low as 0.5 μm) than with the laser spectrometry (as low as 0.1 μm). Determining material porosity on line is a relatively new process. Software exists to optimize process parameters. Material recycling may occur with implementing a vacuum dust system.

These improvements can enclose the process, making throughput higher and decontamination efforts much lower, reducing worker exposure and contaminated waste. The initial cost for equipment and start-up will be higher and the complexity is greater than current operations.

6. ALTERNATIVE EVALUATION

The Pu-238 Alternatives Trade Study Committee met April 21-24, 2008, in Idaho Falls, Idaho, to review and discuss alternatives for granule production and pellet production. The committee first focused on discussing and prioritizing processes for producing a granular form of Pu-238 directly from a solution. Then participants discussed and prioritized processes for converting Pu-238 granules to pellets. They considered integrating granule production with pellet production to form a unified process. The team holds technical expertise in the process alternatives identified for discussion. Committee members are named in Appendix G.

6.1 Granule Production

6.1.1 Alternative Definition

After reviewing the objectives of the evaluation, the technical experts presented nine alternatives for producing a granular/solid form of Pu-238. The alternative methods are discussed in Sections 5.1 and 5.2 and summarized below:

1. **Current process**–The current process employed at LANL uses oxalate precipitation to solidify material, ball milling into powder, and green pressing for granulation.
2. **Improved oxalate precipitation**–This process eliminates the ball milling and grows granules adequate for pressing during precipitation.
3. **Hydroxide precipitation**–Process used at Mound Plant in the 1970's to solidify material. This approach generates small amounts of dust compared to ball milling.
4. **Carbonate precipitation**–Another alternate precipitation method.
5. **Modified direct denitration**–A direct conversion of nitrate to oxide within a rotary kiln.
6. **Granat flocculation**–New hydroxide precipitation method that makes improvements on the Mound process.
7. **Resin bead loading and calcination**–Uses the ion-exchange process for loading Pu onto resin, then calcining the resin to oxide granules.
8. **External Sol-gel granules**–Process for producing very round spheres of precise size.
9. **Spherizator particle production**–Alternate method for producing spheres.

Technical experts presented information on each of the alternatives. Comments from committee members were captured electronically and are included in Appendix G.

6.1.2 Criteria Development

The criteria developed to evaluate the alternatives for producing a granule include:

- **Minimize hazards**–Reduce radiation exposure, improve contamination control, and eliminate production of fine powder
- **Simplify process**–Favor a robust process with fewer process steps and less equipment
- **Minimize technical risk**–Reduce the probability of producing and qualifying flight-approved pellets
- **Control granule process**–Control particle size distribution and ceramic activity and improve the consistency of granule quality
- **Maximize chemical purity**–Maximize chemical purity of the granules.

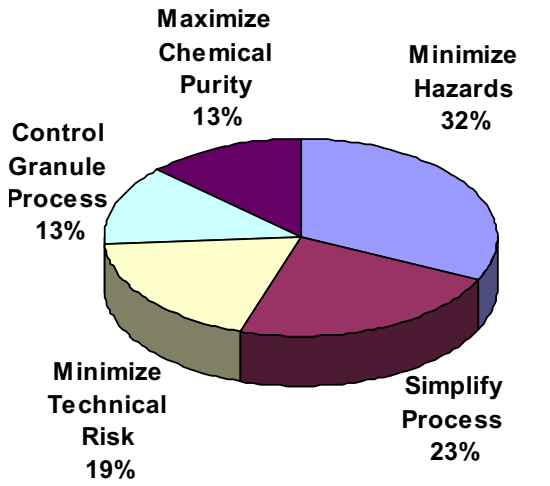

Figure 6-1. Weighted criteria for evaluation of granule production.

6.1.3 Alternative Evaluation

A decision-analysis process using computer-aided facilitation defined the objectives, identified and weighed criteria for process selection, defined alternatives for evaluation, and evaluated alternatives against each weighted criterion. Members scored alternatives against the weighted criteria. Highest scoring alternatives were identified. The risk associated with the highest scoring alternatives were identified and rated for probability and seriousness of the consequence relative to risk. The probability and seriousness were rated as high, medium, or low. Appendix G documents the identified criteria, assigned weight, and scoring of alternatives against the criteria.

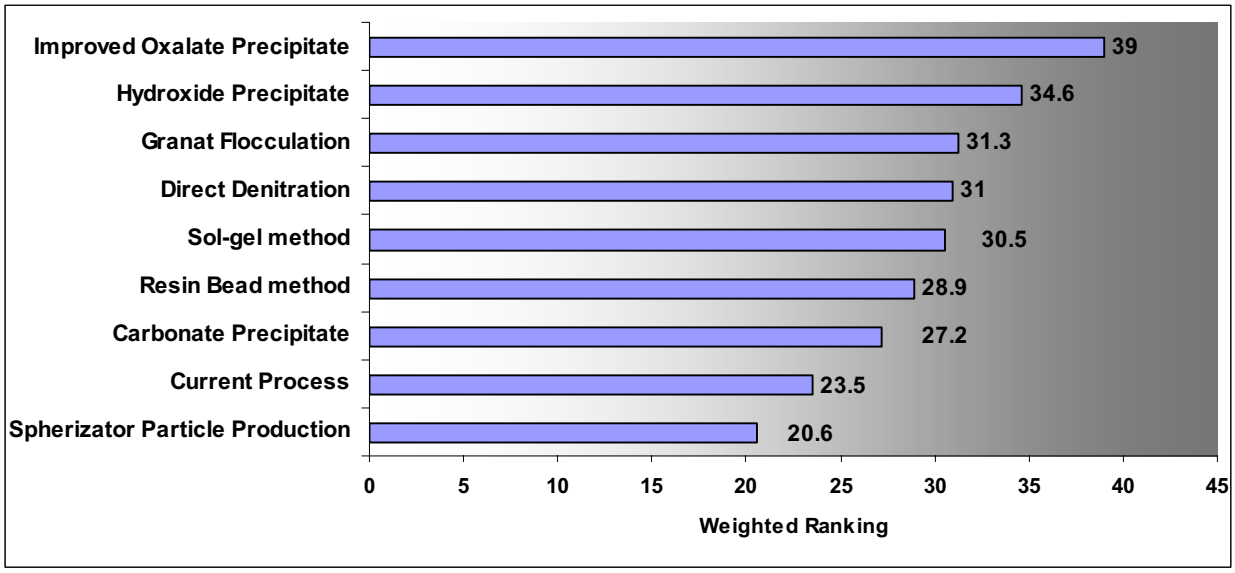

Figure 6-2. Weighted scoring of granule production alternatives.

6.2 Pellet Production

6.2.1 Alternative Definition

Five alternatives were presented for discussion. The presentations on pellet production processes included: (1) the current hot press pellet production, (2) improved hot press pellet production, (3) liquid phase sintering, (4) reaction bonded, and (5) direct sintering. Discussion on the direct sintering resulted in transforming one process into three: pressureless sintering, spark plasma sintering, and super plastic forming.

Flow charts were presented for the resulting seven alternatives that would be evaluated. Section 5.3 provides the flow charts and process descriptions. A summary of the alternatives is provided below.

1. **Current hot press**–The current process employed at LANL blending low- and high-fired granules, hot pressing to shape and density, and then sintering to remove activity.
2. **Improved hot pressing**–New mold materials reduce material interaction, allowing one-step sintering within the hot press.
3. **Liquid phase sintering**–All granules are high fired, mixed with liquid, cold pressed to 65% density, and then sintered to final target 86% density.
4. **Reaction bonding**–Reduce granules to Pu_2O_3, then while pressing, reoxidize to PuO_2, bonding the granules.
5. **Isostatic press/sintering**–Dry-bag isostatic pressing a low-fired green pellet, then sinter at high temperature.
6. **Spark plasma sintering–**Blend low- and high-fired granules and use electrical current to bond and sinter the pellet.
7. **Superplastic forming–**Blend only high-fire granules containing small grain sizes and use reduced temperature hot pressing to deform and bond granules.

6.2.2 Criteria Development

The granule production criteria provided a starting point for developing the following six criteria for the pellet production process:

- **Minimize hazards**–Same criterion as granule
- **Simplify process**–Same criterion as granule
- **Minimize technical risk**–Same criterion as granule
- **Control pellet process**–Ability to control dimensions of the postsintered pellet
- **Improve pellet integrity**–Ability to reduce pellet cracking
- **Maintain microstructure**–Ability to produce pellets that match the current microstructure.

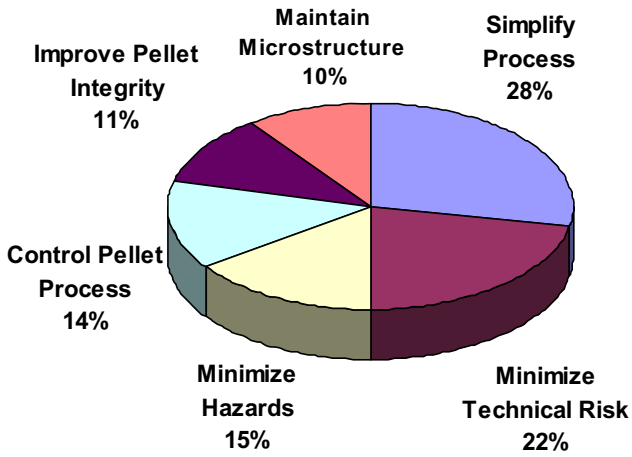

Figure 6-3. Weighted criteria for evaluation of pellet production.

6.2.3 Alternatives Evaluation

The criteria were assigned a weight factor and the same process was followed as in evaluating the granule production. The results of scoring alternatives against the weighted criteria and the associated risk analysis are included in Appendix G.

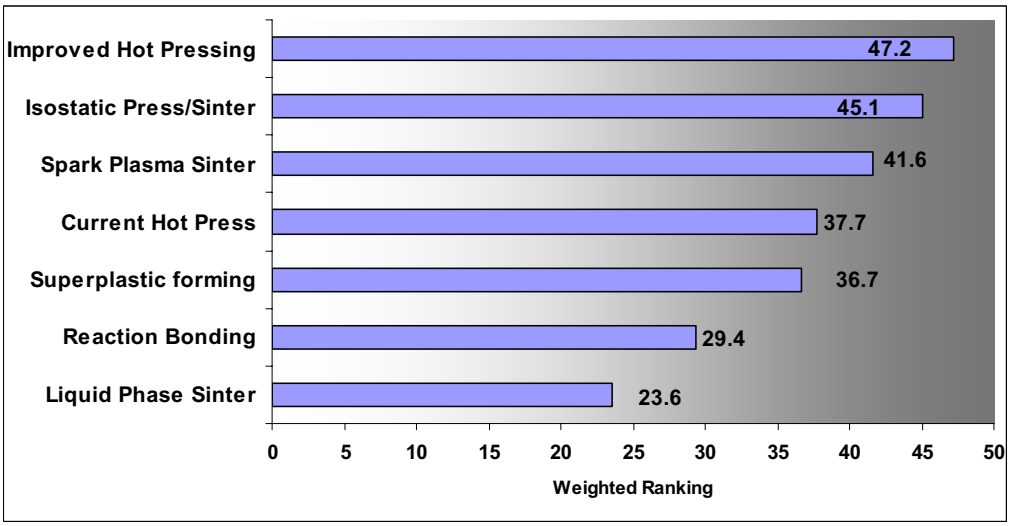

Figure 6-4. Weighted total scores for each pellet production alternative.

6.3 Integration of Results

The committee evaluated pairing the granule production processes with the pellet production processes to define an optimum integrated process. The committee found that most of the granule production processes would work with any of the pellet production processes. An insufficient knowledge of how Pu-238 would work in each process prevented optimizing a single solution. The evaluation shows the improved oxalate precipitation process and the improved hot pressing pellet production are the committee's primary recommendations. These improved processes have the greatest experience base with Pu-238 and the lowest risk of qualifying pellets for space flight. However, other technologies offer potential benefits above these primary recommendations. These alternate technologies should undergo preliminary testing, (with cold surrogates or Pu-239 material) to prove or disprove the potential benefits. The committee recommends the alternatives be grouped based on equipment needs and research applied to a group of alternatives, rather than a specific alternative, as follows:

Granule Production Processes

- Precipitate including oxalate, hydroxide, Granat and carbonate
- Modified Direct Denitration
- Resin loading and calcination.

Pellet Production Processes

- Hot pressing including spark plasma and superplastic forming
- Isostatic pressing and pressureless sintering.

The committee agreed the first research effort should be focused on GPHS characterization, literature searches of the existing information across the DOE complex and internationally, and testing with surrogates. The most promising processes would then be tested with Pu-238.

7. TESTING AND MODELING REQUIREMENTS

Granule production and pellet production methods down selected during the Pu-238 Process Alternative Trade Study of April 21–24, 2008, yielded a number of alternative processes that have high potential of achieving the stated goals of this report, namely to reduce or eliminate formation of fine $^{238}PuO_2$ particles, to improve pellet integrity, and satisfy impact test performance. A number of these methods are variations to the current process; others are novel to Pu-238 heat source production. Systematic experimental and theoretical investigation is required before further down selection of a process alternatives. This section describes a suggested experimental strategy using nonradioactive surrogates and radioactive (Pu-239, uranium, or thorium) surrogates to allow down selection of the most favorable alternatives for Pu-238 testing. Critical technical uncertainties are described for each alternative. These uncertainties can be addressed only during testing, which is why the evaluation committee could not dismiss more alternatives.

7.1 Testing Strategy

The experimental strategy progresses through three phases of testing, with another down select evaluation at the end of each phase as shown in Figure 7-1. Phase I testing will be performed with cold surrogates. Phase I will test the alternatives identified in Section 6.3 because of their potential to successfully produce viable pellets. To direct granule production, additional product information is needed on the current GPHS granules. LANL can obtain the data through additional sampling and characterization as part of their normal pellet production campaign. During this initial phase, an exhaustive literature search should be performed. While a literature search was performed for this evaluation, it was limited by the available time. Even as the report was nearly finished, additional paper copies of Mound testing were discovered. Additional literature searches are useful for the researchers and for the RPS program to uncover more information about development testing in early stages of the program. Testing should begin with granule production work. Pellet production tests would follow several months later. A lag start of pellet testing is necessary to allow time to produce pellet feed material from the granule testing. Initial impact testing of cold surrogates is justified when compared to the cost of impact testing of radioactive material. When Phase I concludes a similar evaluation to the one documented in this report should be performed. The evaluation would consider any additional literature discovered, and the test results, and judge the relative merit of the alternatives. Any alternative that has been demonstrated unworkable for GPHS production would be eliminated from proceeding to Phase II testing. In parallel with

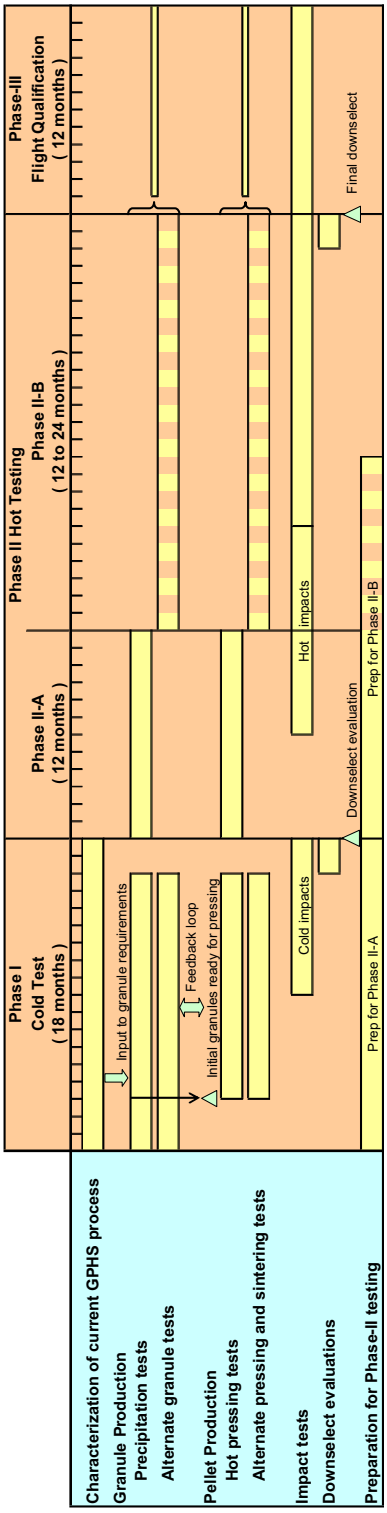

Figure 7-1. Timeline for phased testing program.

Phase I testing, facilities should begin preparations for Phase II testing. Preparations include equipment procurement and installation, safety analysis, and readiness assessments. For nuclear facilities, this preparation can take longer than the test phase. Preparing for Phase II testing while Phase I testing is under way will save time.

The second phase of testing will be performed with radiological material. Initially, Pu-239 may be used, followed by testing with Pu-238. Phase II testing can begin with alternatives that improve on the current processes, precipitation and hot pressing. This testing is represented in the figure as Phase II-A. The other alternatives will require additional preparation activities including new equipment and safety analysis. Depending on the complexity of the process and the introduction of new hazards, additional preparation work may take 1 to 2 years as shown in Phase II-B. These costs are justified only if surrogate testing demonstrates an equivalent benefit over the current process. Also, there is more uncertainty in this phase because we do not know how many alternatives will pass Phase I testing. At the end of Phase II, another down select evaluation will be performed to select the final preferred alternative.

The third phase of testing is flight qualification testing. The extent of testing will be determined by how significant the preferred alternative deviates from the current process.

7.2 Alternative Granule Formation Methods

Down selected alternative granule formation methods include precipitation methods, resin bead loading, sol-gel microsphere, and direct denitration. The selected precipitation methods are variations to traditional plutonium oxalate or hydroxide processes that have been flight tested. Resin bead loading, sol-gel microsphere, and direct denitration have never been applied to Pu-238 GPHS production, but have positive attributes for this study's stated goals and merit further study. The goal of investigating alternative granule formation methods is to form and analyze granules produced by each down selected method, and to systematically compare measurable granule characteristics. From this comparison, further down selection will be performed and the most promising alternatives will be tested with Pu-238 material.

In general, favorable granule characteristics are:

- Granule size distribution from 50 to 250 μm diameter with a mean diameter of 125 μm, and no fine particles (<20 μm).
- A well formed, spherical granule comprised of tightly bonded crystals or aggregates
- A granule with open porosity that retains porosity after heat treatment, has a high tap density, and results in a final pellet theoretical density of ~ 85 to 90%
- A granule with medium to high active surface area
- A chemically pure granule.

To properly evaluate granule product produced by each selected alternative method, a minimum of the following characterization capabilities will be required:

- Particle size analysis
- Surface area analysis
- Pore and density determination
- Optical metallography and electron microscopy
- X-ray diffraction
- Trace elemental analysis.

7.2.1 Granule Formation by Precipitation

Experimental evaluation of all down selected precipitation methods can be accomplished using a single, multipurpose precipitator that will allow for precision process-parameter control and in situ particle growth analysis. Precipitation processes will be monitored in real time to determine the optimal processing conditions of: feed rate, temperature, agitation cycles, digestion rates, and particle size and distribution ranges. Product will be collected for further analysis to determine granule density, porosity, active surface area, crystal structure, surface morphology, and chemical purity.

Technical uncertainties with precipitation require further testing. Initial questions that must be answered to determine the applicability of precipitation for GPHS granule production are:

- **What is the particle size distribution in the precipitant and the granulate produced with the optimized process?**
- **Are there any distinguishing characteristics, for example impurities, between the various precipitation methods?**

7.2.2 Testing Strategy for Modified Direct Denitration

The MDD approach of producing granules has potential benefits above the improved oxalate precipitation approach. The direct denitration process is a simpler process requiring one system to go directly from liquid feed to a finished granule. The approach reduces material handling because it is self-contained.

Technical uncertainties with MDD require further testing. Initial questions that must be answered to determine the applicability of MDD for GPHS granule production are:

- **What is the particle size distribution in the granulate that can be produced by the optimized MDD process?**
  Questions regarding the maximum granule size, the range of granule sizes and the type of size distribution, (Poisson, binomial, continuous uniform or other), are important to optimizing the packing density of granules for pressing. The denitration occurs in a rotary kiln. The evaluation committee's concern is that soft agglomerates will tend to break up, releasing 1-5 μm crystallites during the tumbling process.

ORNL has extensive experience with MDD for producing UO_2 and limited experience in producing $^{239}PuO_2$. However, the output granule requirements for the existing process are different than what is needed for GPHS pellets. Preliminary testing could answer the fundamental questions above. With this information, the MDD method could be further compared to other granulation methods in selecting the best method for producing GPHS pellet feed material. Most important is determining the amount of fine powder produced, because eliminating fine powder is one of the two primary objectives of this evaluation.

Preliminary testing could be performed with cold surrogate material. The required equipment includes a rotary kiln and particle characterization capability discussed above. ORNL currently has the required equipment and could perform the preliminary testing using Pu-239 material following cold surrogate testing.

7.2.3 Testing Strategy for Resin Bead Loading and Calcination

The resin bead approach of producing granules has potential benefits above the improved oxalate precipitation approach. The resin bead method can accurately control the size of granules produced. As discussed in Section 5.3, the granule size distribution controls the packing (tap) density of granules before pellet pressing. By optimizing the granule size distribution, higher tap densities can be achieved. High tap densities require less compaction during pressing and improve stress distribution in the final pellet.

The initial technical uncertainties with this approach can be answered with cold surrogate testing. These initial questions must be answered to determine if the resin bead method will work for GPHS granule production. They are:

- **Can the required chemical impurity be achieved using this method?**
  One of the committee's concerns with the resin bead approach is residual chemical impurities left when reducing the resin material. Increasing the temperature to improve chemical purity will have a detrimental affect on the granule's ceramic activity. Alternate resin materials may reduce the chemical impurities left after resin calcination.
- **What is the ceramic activity of the final granules produced by the resin bead method?**
  Because resin calcination is a thermal process, the committee's other primary concern is the unintentional sintering of granules during resin calcination. The finished granules must have sufficient activity for bonding during the pressing operation. As granule size increases, chemical impurity or the amount of sintering required to achieve chemical impurity may worsen.
- **What is the particle size distribution in the granulate produced by this optimized process?**
  Experience has demonstrated the resin bead method does not produce fine powders. However, the broken microspheres from calcining will produce fine powder. Experimental data should be collected to confirm that powder production is minimal.

ORNL has extensive experience with the resin bead method for Cm-244 sphere formation for radioisotope target production. As with the MDD process, the output granule requirements for the existing process are different than what is needed for GPHS pellets. Preliminary testing could answer the fundamental questions above. Test results should confirm the viability of the resin bead method as an alternative for production of green granules. If pellet production experiments identify the preferred granule feed is only highly sintered granules, then the resin bead method may be the optimal one for producing granules.

Preliminary testing could be performed with cold surrogate material. The required equipment includes an exchange column, calcining furnace, and particle characterization capability discussed above. ORNL currently has the required equipment and could perform the preliminary testing using Pu-239 material following cold surrogate testing.

7.2.4 Testing Strategy for Sol-gel Granule Production

The Sol-gel approach of producing granules has potential benefits above the improved oxalate precipitation approach. The Sol-gel process is a simpler process requiring one system to go directly from liquid feed to a finished granule. The approach reduces material handling because it is self-contained.

Technical uncertainties with Sol-gel require further testing. Initial questions that must be answered to determine the applicability of Sol-gel for GPHS granule production are:

- **What is the particle size distribution in the granulate that can be produced by the optimized Sol-gel process?**
  Broken microspheres from calcining will produce fine powder. Experimental data should be collected to confirm that powder production is minimal.
- **What is the ceramic activity of the final granules produced by the Sol-gel method?**
  Because the microsphere calcination is a thermal process, the committee's other primary concern is the unintentional sintering of granules during calcination. The finished granules must have sufficient activity for bonding during the pressing operation.
- **Can the required chemical impurity be achieved using this method?**
  One of the committee's concerns with the Sol-gel approach is residual chemical impurities from the process chemicals.

Preliminary testing could be performed with cold surrogate material. The required equipment includes a Sol-gel system. ORNL currently has the required equipment and could perform the preliminary testing using Pu-239 material instead of a cold surrogate.

7.3 Pellet Formation Experiments

Down selected alternative pellet production methods include hot pressing and isostatic pressing followed by pressureless sintering. The selected hot pressing methods are variations to traditional hot pressing with new materials and electrical current to improve bonding. Dry-bag isostatic pressing has never been applied to Pu-238 heat source production, but has positive attributes for improving pellet integrity and merits further study. The goal of investigating alternative pellet production methods is to press and analyze pellets, produced by each down selected method, and to systematically compare measurable pellet characteristics. From this comparison a final down selection will be performed and the most promising alternative will be tested further with Pu-238 material.

In general, favorable pellet characteristics are:

- Dimensional accuracy of finished pellet to within +/- 0.23 mm diameter and +/- 0.38 mm length
- Dimensional stability so that shrinkage during sintering does not exceed +/- 0.5%
- Pellet with a final theoretical density of 85-90%
- Grain size between 10 and 30 μm
- A grain porosity consistent with current space flight pellets.

To properly evaluate pellets produced by each selected alternative method, a minimum of the following characterization capabilities will be required:

- Dimensional analysis
- Stoichiometry analysis
- Pore and density determination
- Optical metallography and electron microscopy
- Fracture toughness
- Trace elemental analysis.

7.3.1 Improved Hot Pressing

Potential improvements can be made to the current hot pressing operation for producing pellets. Some improvements such as reducing the compaction ratio are controlled by the input feed material. Other improvements such as reducing die and pellet-oxygen interaction can be influenced by the press design and operation. Pressing operations will be monitored to determine the optimal process parameters for compaction force and rate, press temperature cycle and range, and sintering temperature cycle. Completed pellets will be analyzed for performance attributes including chemical purity, TD, porosity, stoichiometry and fracture toughness.

Attributes of hot pressing that can be improved include:

- **Determining the optimal granule size and distribution**
  Current granulation methods achieve a tap density of approximately 4.0g/cc or 35% TD. Reaching target 86% TD requires a compaction ratio of 2.5. By optimizing the granule size and distribution, density closer to 60-70% can be achieved, reducing the compaction ratio to 1.3 or better. Less compaction will create small stress gradients throughout the pellet and should improve pellet integrity.
- **Evaluation of die material and die coatings**
  Material interaction between the pellet and the die mold is considered the primary contributor to pellet cracking. Eliminating oxygen loss during hot pressing may allow pressing and sintering to be performed in one step and produce a higher quality pellet with less cracking.
- **Performance of spark plasma sintering**
  Spark plasma bonding may improve bonding of granules while shortening the time to press a pellet. If the material interaction cannot be solved by changing die materials or adding die coating, reducing the hot press cycle time would reduce material interaction.
- **Correlate computer modeling to pellet microstructure and impact behavior.**
  As the development effort of an alternate Pu-238 process progresses, pellets will require impact testing to confirm process changes have not adversely altered the pellet's performance characteristics. Computer modeling can potentially reduce the number of costly impact tests.

INL and the University of California-Davis have experience and equipment to test hot pressing methods. Preliminary testing can be performed with cold surrogate material. The required equipment includes a spark plasma press and pellet characterization capability as discussed above. A recent cooperative effort for nuclear fuel fabrication has been proposed for U.C. Davis, Penn State University, UNLV, and INL on the subject "Nuclear Oxide Fuel Fabrication and Processing Modeling Utilizing Field Activation and Employing the Spark Plasma Sintering Method." This cooperation includes: Dr. Douglas E. Burkes, (PI – INL); Collaborators: Prof. Zuhair A. Munir (co-PI – U.C. Davis), Prof. Albert E. Segall (co-PI – Penn State University), Prof. Thomas Hartmann (co-PI – UNLV), Dr. Paul Lessing (co-PI – INL), and Timothy Hyde (co-PI – INL).

7.3.2 Dry-Bag Isostatic Pressing/Pressureless Sintering

The dry-bag isostatic press combined with pressureless sintering has potential benefits over an improved hot press approach of producing pellets. The isostatic press is a simpler process of making pellets, allowing rapid production of green pellets and sintering multiple pellets simultaneously in a single furnace run. Isostatic pressing applies pressure equally to all surfaces of the pellet. This approach significantly reduces stress gradients in the pellet and should produce a pellet less prone to cracking.

Technical uncertainties with dry-bag isostatic pressing require further testing. Initial questions that must be answered to determine the practicality of this process for GPHS pellets are:

- **Is the green pellet sufficiently stable for movement to the sintering furnace?**
  This question cannot be answered until tested with Pu-238, but initial evaluations can be performed with surrogate material.
- **Are pore formers and other additives required?**
  Pore formers or other additives may be needed to achieve the proper porosity in the final pellet or aid in bonding the green pellet until sintering. If these are needed, chemical purity may become a concern and have to be verified.
- **Can the required dimensional tolerances be achieved consistently?**
  The granule input feed must be consistent with predictable shrinkage during sintering to meet the dimensional tolerances of the final pellet.

Preliminary testing could answer most of these fundamental questions. With this information, the isostatic pressing could be further compared to the hot pressing method to select the best method for producing GPHS pellets. The required equipment includes an isostatic press with custom GPHS molds, a sintering furnace and pellet characterization capability discussed above. This type of testing could be accomplished by cooperation between the INL and selected universities.

A good possibility for cooperation would be with the Ceramic and Composite Materials Center, a multi-university research center (NSF Industry/University Cooperative Research Center) consisting of Rutgers University, Pennsylvania State University, and the University of New Mexico. Rutgers University emphasizes ceramic processing, including powder processing and densification (sintering). Densification stresses and distortion produced by density gradients have been studied by Profs. David Green, Gary Messing, and Al Segal. Additive removal from consolidated ceramics has been studied by Prof. Richard Haber. Prof. Stephen C. Danforth (Rutgers Department of Ceramic Engineering) is an expert in sintering, hot isostatic pressing, agglomeration, etc. Many ceramic companies and national laboratories have memberships in this research center. This includes Los Alamos National Laboratory, Sandia National Laboratory, Coors Tek, and Saint Gobain.

Another possibility for cooperation is a mini consortium that has been established between Georgia Tech and Florida State University. Prof. Justin Schwartz (professor at Florida State and adjunct professor at Georgia Tech) has B.S., and Ph.D. degrees in Nuclear Engineering (University of Illinois and MIT, respectively). He also has expertise in ceramic oxide processing (including the surrogate materials of ThO_2, CeO_2, and HfO_2). He recently has been working on the pressing and sintering of ThO_2 pellets for use in a thorium fuel cycle and has submitted a proposal to the 2008 Advanced Fuel Cycle R&D opportunity notice.

7.4 LANL Testing

While all of Phase I testing can be performed at universities, Phase II testing, specifically Pu-238 testing, must be performed at a nuclear facility. Only LANL PF-4 facility is authorized to perform granulation and pellet production work with Pu-238. The initial LANL effort should be to characterize the current GPHS process. Additional granule information is needed to guide research on alternate granule production methods. This information can be obtained as part of normal pellet production operations at LANL. Additional sampling and characterization points along the process can aid in further defining target product specification. The existing authorization basis should bound this characterization work.

Concurrent with characterization activities, LANL will need to prepare for Phase II testing. The conservative approach is to prepare only for precipitation and hot pressing tests first because they are incremental changes to the current process. They should require the least amount of safety analysis to implement. Following the down select evaluation at the end of Phase-I, preparation for testing the remaining alternatives will begin.

7.5 Modeling Capability

At this time, a handful of shock physics/high-strain-rate/collapse codes are available for use in the DOE system. Examples include CTH, an Eulerian wave-propagation code from Sandia National Laboratory; Alegra, an Arbitrary Lagrangian-Eulerian (ALE) code also from Sandia; ALE-3D, an ALE code from Lawrence Livermore National Lab; Abaqus/Explicit, a code capable of modeling high-speed, nonlinear, transient response; LS-DYNA, a product from Livermore Software Technology Corporation including Lagrangian, Eulerian; ALE, and smooth-particle hydrodynamics (SPH) formulations; AUTODYN, an explicit and SPH code; and RADIOSS with explicit capabilities. INL is engaged in developing a series of benchmark problems[1,2] for evaluating comparative characteristics of these shock and high-strain rate physics codes for simulation of impact, blast, and other shock phenomena.

INL has recently investigated various constitutive material models in use within DOE and NASA for impact simulation of Pu-238 fuel pellets as part of an ongoing safety analysis of the RSG-55 Radioisotope Stirling Generator project.[3,4] A Johnson-Holmquist ceramics model was employed that incorporates effects of damage on remaining material strength, and bulking during compressive failure. This model yielded deformations in good agreement (see Figure 7-2) with impact test results for BCI-25.

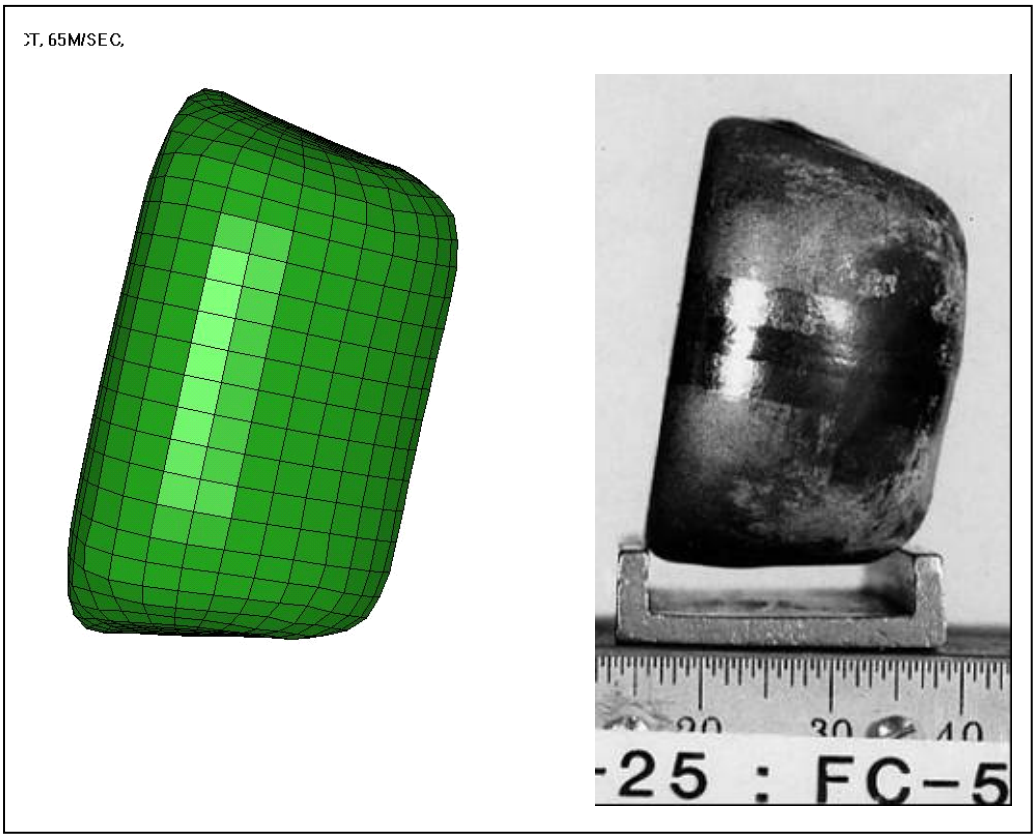

Figure 7-2. Comparison of BCI-25 test specimen (65 m/s onto steel).with numerical simulation, side view.[4]

While good results have been achieved for the bulk response of impacted plutonia pellets, more work is necessary to predict the extent of fracture and resultant particle size distribution in a damaged fuel pellet. Because different pellet-forming processes will yield varying fracture properties and particle size distributions, this modeling effort must be coupled closely with an experimental program to develop constitutive material models and validate the numerical results.

Various high-speed impact test devices[5] are employed to study novel materials at high strain rates and high deformations, both for metallic (ductile) and ceramic (brittle) materials. A simple ballistic impact test device may be employed for either Taylor Anvil testing of metals or dynamic indentation testing of ceramics. These technologies could be reproduced in the appropriate radialogically controlled setting to evaluate candidate plutonia forms.

7.5.1 Modeling Capability References

1. J. M. Lacy, S. R. Novascone, W. D. Richins, T. K. Larson, "A Method for Selecting Software for Dynamic Event Analysis I: Problem Selection," *Transactions 19th International Conference on Structural Mechanics in Reactor Technology*, *August 2007*.
2. J. M. Lacy, S. R. Novascone, W. D. Richins, T. K. Larson, "A Method for Selecting Software for Dynamic Event Analysis II: The Taylor Anvil and Dynamic Brazilian Tests," *International Conference on Nuclear Engineering (ICONE16), Orlando, FL, International Conference on Structural Mechanics in Reactor Technology, May 2008.*
3. W. D. Richins, J. M. Lacy, S. R. Novascone, B. H. Dolphin, "Safety Analysis for a Radioisotope Stirling Generator," *Proceedings of Space Nuclear Conference 2007*, *Boston, Massachusetts, June 2007*.
4. M. B. Sattison et al, *Radioisotope Stirling Generator-55 Watt Interim Documented Safety Analysis*, INL/EXT-07-12251, February 2007.
5. J. M. Lacy, S. R. Novascone, H. S. Chu, "Taylor Cylinder Determination of Impact Material Properties," INL LDRD NS156, 2007-2008.

8. RECOMMENDATIONS

At DOE's request, alternate chemical and mechanical manufacturing methods to produce Pu-238 fueled GPHSs for radioisotope thermoelectric generators were evaluated. These were compared to current processing methods to determine if (1) alternative fabrication processes could reduce the associated hazards, especially the production of respirable fines, and (2) produce an equivalent GPHS product that can be flight qualified. An expert committee performed the evaluation, with additional input from four national laboratories experienced with Pu-238 handling. The objectives of the evaluation were:

Objective 1: Minimize the potential for airborne radioactive contamination release during fabrication.

Objective 2: Reduce personnel radiation exposure during fabrication.

Objective 3: Reduce cracking of the unclad pellets while satisfying impact test and operating performance requirements.

Based on the committee's expertise, the list of process alternatives was winnowed to a small number that warrant further testing as prioritized in Table 8-1.

Table 8-1. Granule and pellet production methods that merit testing.

Granule Production Methods	Pellet Production Methods
Precipitation methods	**Hot pressing methods**
• Improved oxalate precipitation	• Improved hot pressing and sintering
• Hydroxide precipitation	• Spark plasma sintering
• Granat flocculation	• Superplastic forming
• Ammonium plutonyl carbonate precipitation	
Alternate granule methods	**Alternate pressing methods**
• Modified direct denitration	• Preforming and pressureless sintering
• Sol-gel microsphere	
• Resin bead loading and calcination	

The committee developed the following findings and recommendations.

Finding 1 – The existing product specifications are essentially process specifications. Physical characteristics of the GPHS product are not specifically measured and controlled. Rather, the fabrication process and operating parameters are tightly controlled to ensure consistency between new batches and the original product, and thus tie to the flight-qualification database.

The GPHS product specifications have not changed significantly since the 1970s. For this evaluation, the committee attempted to define target granule and pellet specifications based on available data. The physical characteristics of Pu-238 in-process material require additional research if the current process is to be modified.

Finding 2 – Several processes potentially can achieve the objectives. The preferred granule and pellet process alternatives are (a) the improved oxalate precipitation granule production and (b) the improved hot pressing pellet production.

These improved processes are the only alternatives that have been tested by making GPHS pellets with Pu-238 material. The processes are considered incremental changes making significant

improvements to operational safety while minimizing changes to facility safety basis. Because they use the same process technology, the preferred alternatives offer the lowest risk for flight qualification.

Finding 3 – Other alternative processes entail higher risk but offer potentially higher rewards. Further reduction in dust generation, simpler operations and improved stress distributions may be achieved.

Recommendation 1 – Characterization should be performed on the current LANL Pu-238 process to document the physical characteristics of GPHS in-process material and final products as soon as possible.

Any development of a new process requires a more complete product specification. As a first step, during FY-09 pellet production at LANL, additional sampling and characterization should be performed. Pellet production and characterization could be funded as part of a DOE redirection of LANL's RPS infrastructure.

Recommendation 2 – Final selection of a new Pu-238 process should be based on (1) test results from cold surrogate, Pu-239 surrogate, and Pu-238 testing, (2) optimized process parameters that produce the most repeatable product with the highest quality and (3) ability to produce GPHS pellets that can be readily qualified for space flight. The committee therefore recommends a staged test program, eliminating at each stage any processes that do not warrant further consideration.

Recommendation 3 – Investigate the processes identified in the table. Approximately $5 M over a two year period is needed for university/laboratory studies to complete initial cold surrogate testing. Funding would be used to conduct literature reviews, to perform testing, including impact testing, to answer key technical uncertainties; and to further downselect alternatives.

Numerous processes can be grouped as shown in Table 8-1 and tested using the same equipment to reduce testing costs. For example, one precipitation system can be used to test all precipitation methods, and one hot press system can test three methods: improved hot pressing and sintering, spark plasma sintering, and superplastic forming. Each of the other granule and pellet production methods require individual test systems.

Approximately $2.2 million in FY-09 and $2.7 million in FY-10 is needed to complete initial cold surrogate testing. Funding will support university research with laboratory oversight. Oversight is important to ensure results are applicable to the RPS program. The estimated funding split is 80% university funding and 20% laboratory funding.

Recommendation 4 – Prepare for Pu-239 and follow-on Pu-238 testing of the preferred alternatives following down selection of process alternatives. These preparations will require a year or more and can be performed in parallel with surrogate testing.

9. BIOGRAPHIES

Team Biographies for Evaluating Alternatives to the Pu-238 Heat Source Fabrication

INL Contributors

Mark Borland, B.S. Mechanical Engr. Team Lead
Mark served as technical lead for numerous large projects at INL including the Pit-9 GEM Project, the Sandia Debris Bed Treatment Project and Pu-238 Consolidation Project. Mark received a B.S. M.E. from Carnegie-Mellon University in 1984 and is actively pursuing his M.S. in Nuclear Engineering from University of Idaho.

Steve Frank, Ph.D. Chemistry Granule Production Lead
In the INL Pyroprocessing Technology group, Steve is working numerous projects on electrochemical and aqueous processing, material separation, and material characterization. Steve was the target processing technical lead for the Pu-238 Consolidation Project. Steve was also technical lead on the Pu-238 Calcine Waste Form research. Steve received his B.S. in Chemistry from Fort Lewis College in 1984 and his Ph.D. in Chemistry from Washington State University in 1989.

Paul Lessing, Ph.D. Material Science Pellet Fabrication Lead
Tech Lead at INL for Ceramics in the Materials, Properties, and Performance Department for 18 years, Paul is a ceramic processing expert. He was granted the INL Lifetime Achievement Award in Inventorship in 2006 (at the 10 patent level). Paul is currently working on ceramic design issues for pellet fabrication of Global Nuclear Energy Partnership and TRU-MOX fuels. Paul worked at the LANL in the chemistry and fabrication area (CMB-11) during the 1970's on the development program for the $^{238}PuO_2$ GPHS. He has a B.S. in Ceramic Engineering and a Ph.D. in Material Science, University of Utah.

Consultants

Dennis F. Bickford, M.S. Material Science Solidification
Dennis retired from Savannah River National Lab in 2006. He was the Separations Technology manager for Building 235-F Operations during the startup of the Plutonium Fuel Form Facility and during production of the Pu-238 fuel for the Galileo and Ulysses missions. Denny received a B.S.M.E. and B.S. in Metallurgy and Materials Science from Massachusetts Institute of Technology and an M.S. in Metallurgy and Materials Science from Carnegie-Mellon University. Postgraduate studies include Ceramics Engineering at Clemson University. He is a fellow of the American Ceramic Society.

Roger Cannon, Ph.D. Material Science Pellet Fabrication
A university professor from Rutgers (27 years in their Ceramics Department–fellow, American Ceramic Society), Roger has 40 years experience, mostly in ceramic processing (including work at TRW and MIT's Ceramic Processing Lab). He taught a graduate course in Mechanical Properties for 27 years and is coauthor on the second edition of Wachtman's text book on Mechanical Properties. Roger will provide a nonnuclear (industry) perspective to the complexity of fabricating a heat source pellet with specific NASA performance characteristics. He has a B.S. in Ceramic Engineering, University of Utah; and a Ph.D. in Material Science, Stanford University.

Ken Chidester, M.S. Nuclear Engr. Pellet Fabrication
Ken, a LANL retiree (2004) is a plutonium fuels expert and continues to work in that field as a technical consultant. He worked 5 years for Westinghouse Hanford on plutonium and uranium oxide nuclear fuel development for the Fast Flux Test reactor. He joined Los Alamos in 1983 and worked on several uranium and actinide ceramic fuel development programs. This included being the principal investigator

for developing a process to fabricate uranium nitride fuel for space reactors. At Los Alamos, he managed the Advanced Fuels Group that performed reactor fuel development and was a senior staff member of the Pu Science and Engineering Group that produced all the $^{238}PuO_2$ heat sources. He has a B.S. in Ceramic Engineering, University of Utah; and an M.S. in Nuclear Engineering, University of New Mexico.

Tom Wheeler, B.S. Mech. Engr. Powder Handling
Tom worked at the INL developing material handling systems, including custom equipment for the Pit-9 Stage-II project and is knowledgeable in handling Pu powders. He is currently employed at Walsh Eng.

ORNL Contributors

Brian Cowell, M.S. Nuclear Engr. Granule Production
Brian Cowell has 18 years experience at Oak Ridge National Laboratory in the nuclear field, mostly applied to the nuclear fuel cycle, specifically nuclear fuel fabrication and irradiation performance. He currently manages the Russian Plutonium Disposition Program at ORNL. Since 1994, he has been involved in a number of prior reviews of the Pu-238 production and GPHS fabrication processes for development of alternative processes with lower radiological risks. He has a B.S. and an M.S. degree in Nuclear Engineering.

Brad Patton, M.S. Chem. Engr. Granule Production
Brad Patton has more than 30 years experience with separation, purification, and source fabrication in a number of positions at the Oak Ridge National Laboratory (ORNL). His experience at ORNL includes processing and handling highly alpha active actinides (Pu-239, Cm-244, U-233, and Cf-252). Mr. Patton held a leadership role in separation, purification, and source fabrication at the Radiochemical Engineering Development Center at ORNL for a number of years. Mr. Patton holds B.S. and M.S. degrees in Chemical Engineering from the University of Kentucky.

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Facilitators

Linda Seward Facilitator
Linda Seward is a certified value specialist as recognized by the International Society of Value Engineers. Ms. Seward has 30+ years experience in industrial engineering, problem-solving, decision-making meeting facilitation in the DOE environment and private industry. Ms. Seward is currently employed by PS2 Associates in Idaho Falls, Idaho.

William West Facilitator
William West is a facilitator with Polestar Applied Technology, Inc., and has more than twelve years experience in facilitating groups, eight of which were in computer-assisted facilitation. Mr. West worked at the INL from 1997 to 2006, and had 20 years prior experience with Bureau of Land Management (BLM). William received a B.S. in Range & Forest Management and an M.S. in Systems Ecology, both from Colorado State University.

Appendix A

Plutonium-238 Hazards

Appendix A
PLUTONIUM-238 HAZARDS

A-1. INTRODUCTION

Plutonium is the second artificial or man-made element to be discovered and the first to be produced on an industrial scale. Plutonium does occur in nature, at very low concentrations on the order of one part in 10^{11} in pitchblende, owing to cosmic radiation interaction with uranium. The first isotope of plutonium to be discovered in early 1941 was Pu-238 ($T_{½}$ = 87.7 years), which was produced in the 60-in. cyclotron at the University of California at Berkeley. It was produced by bombarding a U-238 ($T_{½} = 4.47 \times 10^{9}$ years) target with deuterons (H-2), producing Np-238 ($T_{½}$ = 2.12 days), which decays by the emission of beta radiation to Pu-238.

$$^{238}U + {}^{2}H \rightarrow {}^{238}Np + 2n$$

$$^{238}Np \rightarrow {}^{238}Pu + \beta$$

The 87.7 year half-life of Pu-238 and its spontaneous fission capability make it an excellent heat source for remote power applications. Unfortunately, the same nuclear properties of plutonium that make it attractive to science also make the element hazardous to human beings.

A-2. MANUFACTURE OF PLUTONIUM-238

Because it is an excellent heat source radionuclide, its manufacture in a more isotopically pure form is highly desired. The current production methodology is to irradiate Np-237 ($T_{½} = 2.14 \times 10^{6}$ years) in a nuclear reactor or a neutron producing accelerator to transmute the Np-237 to Np-238, which then decays through beta emission to Pu-238.

$$^{237}Np + n \rightarrow {}^{238}Np \rightarrow {}^{238}Pu + \beta$$

The neutron fields used to create the Pu-238 can also produce other isotopes of plutonium. The amount of other isotopes generated depends on the irradiation time, neutron flux, and neutron energy spectrum. The heavier isotopes are produced through multiple neutron capture events. Small amounts of the isotope Pu-236 are made through the interaction:

$$^{237}Np + n \rightarrow {}^{236}Np + 2n$$

$$^{236}Np \rightarrow {}^{236}Pu + \beta$$

This isotope is important because of its short half-life, and because decay products produce significant radiations. Using the current practices, heat source plutonium is generated with the following isotopic mix.

Table A-1. Typical isotopic composition for heat source plutonium.[a]

Isotope	Weight Percent	Specific Activity Ci/g	Activity per Gram	Percent of Activity
Pu-238	>82	1.71×10^{1}	1.40×10^{1}	95.7
Pu-239	14.3	6.21×10^{-2}	8.89×10^{-3}	0.060
Pu-240	3.0	2.27×10^{-1}	6.82×10^{-3}	0.047
Pu-241	0.6	1.03×10^{2}	6.19×10^{-1}	0.423
Pu-242	0.1	3.94×10^{-3}	3.94×10^{-6}	2.69×10^{-3}
Pu-236	$<2 \times 10^{-6}$	5.32×10^{2}	1.06×10^{-5}	7.24×10^{-3}

a. Adapted from American National Standards Institute (ANSI) N317, "Performance Criteria for Instrumentation Used for Inplant Plutonium Monitoring." [1]

After the neptunium target has been irradiated, it is processed through a chemical separations process to isolate the plutonium. The plutonium exits this process as plutonium oxide (PuO_2) in a powder form. For use as a heat source material in the space program, the material must meet strict purity standards. So before converting the plutonium into a usable heat source, the material is characterized to ensure that it meets the required specifications. In addition to measuring chemical impurities, the particle size and radiation emission rate is measured. The neutron emission rate after processing must be <6000 n/s-gm Pu-238. To achieve this, an oxygen exchange is performed to exchange the heavier isotopes of oxygen for O-16. It is performed by heating the powder to 775-1000°C and purging with oxygen that has been depleted of O-17 and O-18.

The powder is ground in a ball mill to reduce the particle size from a mass median diameter of about 3.4 μm to 1.2 μm. Particles of PuO_2 with a mass median diameter of 1.2 μm have an aerodynamic median diameter of about 4.0 μm, making them in the respirable range for humans.

The fine powder is formed into granules that are less than 125 μm in diameter. The granules are split into two batches and 60% are treated at 1,100°C while the remaining 40% are treated at 1,600°C. The two batches are combined and mixed in a ball mill, and loaded into a hot press. A pellet is created by hot pressing in a vacuum. The pellet is encased in a welded iridium cladding.[2] All this processing takes place in gloveboxes to protect the workers from the plutonium.

A-3. PHYSICAL AND CHEMICAL PROPERTIES

In the metallic state, plutonium is a silvery-white metal, much like nickel in appearance. Its melting point is 640°C and its boiling point is 3327°C. Plutonium metal has a density of 19.8 g/cm^3. The metal is pyrophoric, so it is usually handled in an inert, dry atmosphere of nitrogen or argon. Of more interest to the current discussion is plutonium dioxide, a dark olive green or yellowish brown powder (depending on form) that has a melting point of 2400°C and a boiling point of 2800°C. Loose powder has a density of about 2.0 g/cm^3 and if pressed and sintered into a pellet, the density can range from 10.3 to 11.0 g/cm^3. As an oxide it is chemically very stable and relatively inert. These properties make the oxide of plutonium the preferred form for shipping and storing.

A-4. NUCLEAR PROPERTIES

There are many plutonium isotopes and all are radioactive. Isotopes with even mass numbers (except mass number 246) are primarily alpha emitters. Isotopes of mass numbers 232, 233, 234, 235, and 237 also decay by electron capture; isotopes of mass numbers 241, 243, 245, and 246 decay by beta emission. Many of the alpha-emitting isotopes, such as Pu-238 and Pu-240, also fission spontaneously and emit neutrons. All of the particle emissions are accompanied by x-ray and gamma-ray emissions over a wide range of energies.

A-4.1 Decay Schemes

The decay modes of Pu-238 and other isotopes and decay products are shown in Table A-2. Only the most abundant radiations have been included in the table; more detailed information can be found in International Commission on Radiation Protection (ICRP) Publication 38,[3] and from the National Nuclear Data Center. Pu-238 is an alpha emitter with a relatively short half-life, making alpha heating a problem for the storage and handling of large amounts of this isotope. The specific activities and decay heats for selected isotopes and decay products are given in Table A-3. Gram quantities of Pu-238 can generate enough heat to melt plastic bags. It must be handled with insulated gloves, and special precautions must be taken to ensure a good thermal heat sink during shipping and storage.

Table A-2. Radioactive decay properties of selected isotopes and decay products, excluding spontaneous fission.

Isotope	Half-life	Mode of Decay Particle	Energy MeV	Yield %	X-ray Energy MeV	Yield %	Gamma Ray Energy MeV	Yield %
Pu-236	2.851 y	α	5.77	69.3	L's 0.011-0.021	13[c]	0.0476	6.6×10^{-2}
		α	5.72	30.6			0.109	1.2×10^{-2}
Pu-238	87.7 y	α	5.50	71.0	L's 0.011-0.021	15[c]	0.0425	3.95×10^{-2}
		α	5.46	28.8			0.0999	7.35×10^{-3}
Pu-239	2.41×10^4 y	α	5.157	73.1	L's 0.0116-0.0215	5.0[c]	0.099	1.22×10^{-3}
		α	5.144	15.0			0.129	6.41×10^{-3}
		α	5.106	11.8			0.375	1.55×10^{-3}
							0.414	1.46×10^{-3}
Pu-240	6564 y	α	5.168	72.8	L's 0.0115-0.0215	10.8[c]	0.0452	4.50×10^{-2}
		α	5.124	27.1			0.104	7.08×10^{-3}
Pu-241	14.35 y	β	0.0052[d]	100.00	—	—	0.077	2.20×10^{-5}
		α	4.896	2.04×10^{-3}			0.1037	1.01×10^{-4}
		α					0.114	6.0×10^{-6}
							0.149	1.9×10^{-4}
		α					0.160	6.71×10^{-6}
Pu-242	3.73×10^5 y	α	4.901	77.5	L's 0.0116-0.0215	9.1[c]	0.0449	3.6×10^{-2}
		α	4.857	22.4			0.104	7.8×10^{-3}
Am-241	432.2 y	α	5.486	85.2	L's 0.0119-0.0222	42[c]	0.0263	2.4
		α	5.443	12.8			0.0332	1.2×10^{-1}
		α	5.388	1.4			0.0595	35.7

(a) Data from Dunford and Burrows (1993).[4]
(b) L's = L x-rays; K's = K x-rays.
(c) Total for all x-rays. The value represents an average obtained from data at Pacific Northwest Laboratory, Lawrence Berkeley Laboratory, and Lawrence Livermore Laboratory.
(d) Average beta energy given. The maximum beta average for Pu-241 is 0.0208 MeV.

Table A-3. Specific activity decay heats of selected isotopes.[a]

Isotope	Half-life Y	Specific Activity, Ci/g	Average Particle per Disintegration	Energy MeV[(b)]	Decay Heat W/g[(b)]
Pu-236	2.851	α 532	α	5.75	13
Pu-238	87.7	α 17.1	α	5.49	15
Pu-239	2.407×10^4	α 6.22×10^{-2}	α	5.14	5.0
Pu-240	6564	α 0.229	α	5.16	10.8
Pu-241	14.35	α 2.52×10^{-3}	α+β	5.27×10^{-3}	3.29×10^{-3}
		β 103			
Pu-242	3.733×10^5	α 3.93×10^{-3}	α	4.90	1.16×10^{-4}
^{2}Am-241	432.2	α 3.43	α	5.37	0.115

(a) Data from ICRP 38 (1983).[3]
(b) Includes atomic recoil and low-energy x-ray production.

While Pu-241 is a beta emitter, its low maximum energy of 0.02 MeV and average energy of 0.005 MeV reduce the beta's range to less than the dead layer of skin. This eliminates it as an external hazard and therefore it is only an internal hazard. Of more importance, Pu-241 decays to Am-241. So over time there will be a buildup of Am-241 in the heat source or the heat source processing equipment. Am-241 has a 60 keV photon that can be an external radiation hazard especially in containments with little shielding, like gloveboxes.

The plutonium isotopes emit relatively few high-energy photons and because of the high density of plutonium, many photons are self-absorbed. In some instances, the decay products may become significant in radiation protection. For instance, the isotope Pu-236 often constitutes a fraction of a percent of the plutonium mass. However, if the plutonium is shielded, the decay products of Pu-236 may be the largest contributors to exposure. Pu-236 decays through a chain of nine daughter products to reach stable Pb-208. See Figure A-1 for the Pu-236 decay chain.

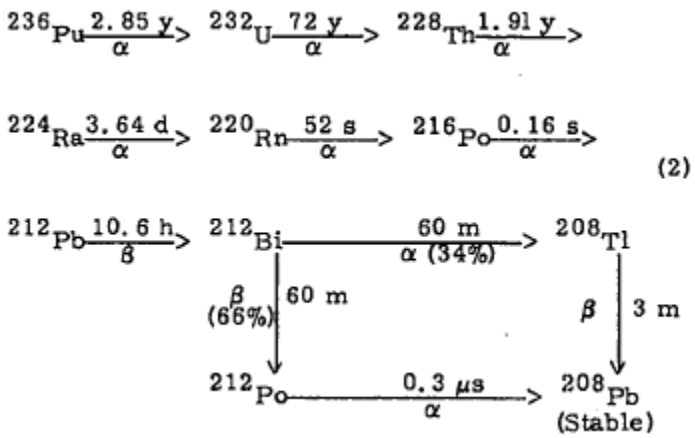

Figure A-1. Pu-236 decay chain.

Activity of the Pu-236 daughters increases steadily after the plutonium separation until it peaks at about 18 years later. The most significant of these radiations are from Pb-212, Bi-212 and Tl-208. The photons energy and abundance is given in Table A-4 below. The percent abundance as given in Table A-4 refers to the number of photons per 100 disintegrations of Th-228. This convention is used because these short-lived daughters are seen in equilibrium with Th-228 and are due to the branching decay of Bi-212.

Table A-4. Principal gamma ray abundances from Pu-236 daughters.

Nuclide	Gamma, Mev.	% Abundance
^{212}Pb	0.239	82
^{212}Bi	0.727	6
^{208}Tl	0.277	3
	0.511	8
	0.583	30
	0.860	3
	2.62	34

The three most abundant gamma energies are from Pb-212 and Tl-208, and can contribute the most to the total photon flux from Pu-238 heat source product. Table A-5 shows intensity growth after plutonium separation owing to these gamma rays.[5]

Table A-5. Growth of Pb-212 and T1-208 gamma activity.*

Time After Purification, years	^{212}Pb, 0.239 Mev., photons/sec.	^{208}Tl, 0.583 + 2.62 Mev., photons/sec.
0.1	330	260
1.0	27,000	21,000
2.0	90,000	70,000
5.0	330,000	260,000
10.0	570,000	450,000
18.0 (max.)	660,000	510,000

* For 1 gram of plutonium-238 product containing 1.2 ppm ^{236}Pu.

In plutonium that contains a few weight percent Pu-241, the Am-241 decay product is important because it emits a large number of 60-keV photons. These photons are less penetrating than those of the Pu-236 daughter products, yet they can be a significant source of exposure to the hands and forearms when handling plutonium in gloveboxes. The fractional amount of Am-241 produced by beta decay from Pu-241 is given as a function of time since chemical separation (see Figure A-2).

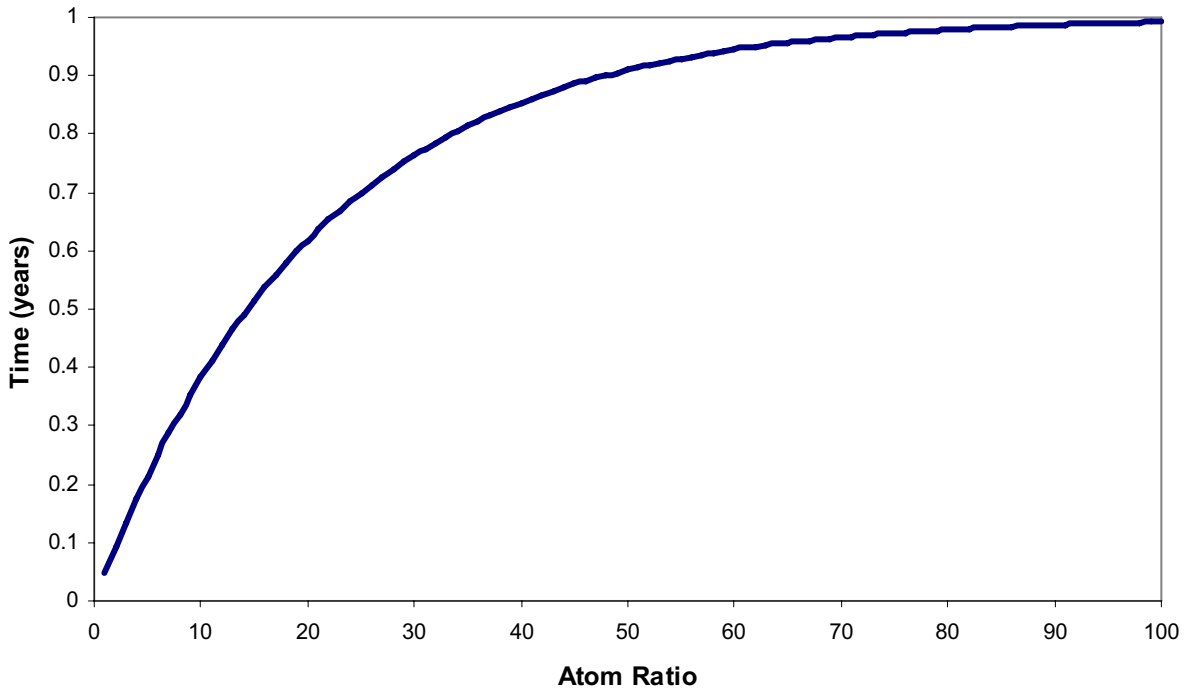

Figure A-2. Atomic ratio of Am-241 to Pu-241 (t=0) produced by the beta decay of Pu-241 as a function of time since chemical separation.

A-4.2 Neutron Yields and Spectra

Plutonium-238 also emits neutrons from spontaneous fission and from alpha-neutron reactions with light elements. The spontaneous fission half-life and the neutron yields from spontaneous fission and alpha-neutron reactions for plutonium are discussed in this section. The approximate neutron yield from a substance with a known isotopic composition can be determined by adding the contributions from each component.

A-4.2.1 Spontaneous Fission Neutrons

Several radionuclides exhibit the capability of spontaneous fission. That is, the nucleus of the atom will fission without any outside forces acting upon it. The fissioning nucleus releases approximately 200 MeV of energy with most of this being transferred to the fission fragments as kinetic energy. Pu-238 on average also emits 2.33 neutrons per fission. The spontaneous fission yields of radionuclides of interest are given in the Table A-6.

Table A-6. Spontaneous fission neutron yields.

Isotope	Total Half-life	Spontaneous Half-life Years	Spontaneous Fission Yield, n/sec-gram
Pu-238	87.74 y	4.77×10^{10}	2.59×10^{3}
Pu-239	2.41×10^{4} y	5.48×10^{15}	2.18×10^{-2}
Pu-240	6.56×10^{3} y	1.16×10^{11}	1.02×10^{3}
Pu-241	14.35 y	2.5×10^{15}	5×10^{-2}
Pu-242	3.76×10^{5} y	6.84×10^{10}	1.72×10^{3}
Am-241	433.6 y	1.05×10^{14}	1.18

A-4.2.2 Alpha–Neutron Reactions

Alpha particles emitted from plutonium and other radionuclides have enough energy to overcome the coulomb barrier in low atomic number elements and create unstable nucleus that can emit neutrons. Because of the high specific activity of Pu-238, this can be a significant source of neutrons. Of special interest is the following reaction in plutonium oxide.

$$\alpha + {}^{18}O \rightarrow {}^{21}Ne + n$$

Table A-7 provides the alpha neutron yields for oxides of the radionuclides found in Pu-238.

Table A-7. Neutron yields from alpha-neutron reactions for oxides and fluorides.

Isotope	Alpha Decay Half-life	Alpha Yield α/s-g	Average Alpha Energy MeV	α,n Yield in Oxides n/s-g
Pu-238	87.74 y	6.4×10^{11}	5.49	1.34×10^{4}
Pu-239	2.41×10^{4} y	2.3×10^{9}	5.1	3.81×10^{1}
Pu-240	6.56×10^{3} y	8.4×10^{9}	5.15	1.41×10^{2}
Pu-241	5.90×10^{5} y	9.4×10^{7}	4.89	1.3
Pu-242	3.76×10^{5} y	1.4×10^{8}	4.90	2.0
Am-241	433.6 y	1.3×10^{11}	5.48	2.69×10^{3}

Oxygen-18 makes up only 0.2% of oxygen in nature. Even though this is a small percentage, the neutron emission rates can be reduced in oxides by exchanging the O-18 atoms with O-16 and reducing this percentage to as low as possible. This exchange is performed at several stages in the development of heat sources used for deep space applications.

In addition to oxygen, trace impurities of other light elements can significantly affect the neutron emission rate owing to alpha neutron reactions. Table A-8 provides the neutron yields from trace impurities in plutonium.

Table A-8. Specific neutron yields form light element impurities.

Element	Neutrons Per Second for one Part per Million
Li	4.6
Be	133
B	41
C	0.2
N	0.0 (α, n threshold too high)
O	0.1
F	18
Na	2.2
Mg	2.1
Al	1.0
Si	0.2
P	< 0.03
S	< 0.03

A-5. OCCUPATIONAL HAZARDS

Personnel working with plutonium are exposed to gamma rays, x-rays, and neutrons, as well as possible uptake into their body. The external radiation hazards are significant and should be reduced to as low as reasonably achievable by reducing the time personnel are exposed to the radiation fields; increasing the distance from the radioactive material and personnel; using shielding to reduce the intensity of the radiation; and reducing the radiation source term through appropriate decontamination. The internal radiation hazard results from the emission of alpha radiation and the high specific activity of Pu-238, which results in higher doses from smaller quantities of material than radionuclides having longer half-lives.

A-5.1 Chemical Versus Radiological Hazards

The radiological toxicity of Pu-238 far exceeds the chemical toxicity of this heavy element. The oxide form is extremely stable and its low solubility in near-neutral or basic solutions reduces the uptake through ingestion by a factor >1000 compared to other plutonium compounds, such as the citrate or ethylenediamine tetraacetic acid complex. Tipton[6] summarizes the differences in chemical hazards between plutonium and uranium: “In contrast to uranium, the chemical toxicity of plutonium is insignificant in comparison to the hazard arising from its natural radioactivity.” Acute toxicity has never been observed in man for plutonium and epidemiologic studies have not produced positive results of toxic effects.

A-5.2 Radiological Hazards

The importance of identifying the hazards from plutonium was recognized as soon as significant quantities of the material were available. Studies have been conducted of its metabolism and organ distribution as well as acute toxicity in several species of animals. Human studies include those who were directly injected with plutonium, workers who received uptakes from occupational exposures as well as accidents, and the general public from fallout from nuclear weapons testing. From this testing, the biological bases for establishing the values of maximum permissible concentration of plutonium in air and in water were established.

A-5.2.1 Modes of Entry into the Body

Plutonium may enter the body through four different routes: through inhalation, through injection, through ingestion, or through absorption through intact skin. These pathways may occur singly or in any combination.

- Inhalation is the breathing in of particles of plutonium. Particles are considered respirable if their aerodynamic diameter is 10 μm or less. Inhalation is the probably the most prevalent mode for occupational intake of plutonium.
- Injection is potentially the most serious mode of intake because of the high dose-per-unit uptake of plutonium. Injection occurs in wounds that are a result of direct penetration by an object (i.e., a puncture or cut), of abrasion, or of burning by an acid, caustic, or thermal source.
- Ingestion of plutonium poses a relatively small risk because the uptake factor from the GI tract to the blood is quite small and because most of the alpha energy from transformations within the GI tract is absorbed by contents of the GI tract, rather than by the target tissues of the tract itself.
- Absorption of plutonium through intact skin is almost nonexistent. During skin decontamination, care must be taken to ensure that the skin integrity is not damaged. If the skin integrity is lost, the resulting wound could become a source of uptake.[7]

A-5.2.2 Distribution Within the Body

As a result of the extensive study on plutonium metabolism, the ICRP has promulgated biokinetic models for the internal distribution and retention of plutonium. The most recent model was described in ICRP 60.[8] The model is similar to previous models with regard to the organs of significance, but differs with regard to the fraction of uptake deposited in the organ and its respective retention (or clearance) half-time in the organ. Once plutonium reaches the bloodstream, it is translocated primarily to the liver and skeleton. In the skeleton, it is deposited primarily on the endosteal surfaces of mineral bone, from which it is gradually redistributed throughout the bone volume by resorption and burial. Because of the extremely slow nature of this redistribution, plutonium is considered to be uniformly distributed over bone surfaces at all times following skeleton deposition. A small fraction of the translocated plutonium reaches the gonads. Although the gonadal fraction is different for males and females, the calculated gonadal doses are the same regardless of gender because the plutonium concentration in the tissues is assumed to be the same. The ICRP assumes that the remainder goes directly to excretion. Although the ICRP did not specifically state the fraction of systemic excretion occurring by urine as opposed to feces, a 0.5 fraction for each is often assumed.

A-5.2.3 Role of Specific Activity on Physical/Chemical Behavior

Plutonium oxide is a very stable compound and would not normally be considered soluble in water and aqueous solutions. However, research has shown that PuO_2 solubility is not zero and there is a difference in the rates of dissolution between $^{238}PuO_2$ and $^{239}PuO_2$ which was thought to be due to the higher specific activity of the $^{238}PuO_2$. The measured the dissolution rate in a neutral aqueous solution is 100 ng m^{-2} s^{-1} for Pu-238 and is only 1 ng m^{-2} s^{-1} for Pu-239. These rates of dissolution are small and dependent on factors such as the pH, temperature, the presence of oxidizing, reducing or complexing agents, the surface areas of the particles, and the history of the sample.

Two mechanisms have been hypothesized to account for this phenomenon. First, a model based on aggregate recoil was suggested in which the nuclei that recoil during alpha decay eject or are accompanied by atoms or groups of atoms. A second model was suggested in which the damage trails produced by the recoiling nuclei are attacked preferentially by the lung fluid leading to accelerated dissolution rates.

In the first model, subparticles would be produced as recoil aggregates whereas colloidal reaction products would be produced by the second. The differences in "dissolution rates" between $^{238}PuO_2$ and $^{239}PuO_2$ were postulated to be controlled by radiation damage and that alpha decays occurring near the surface of the particle ejected a certain number of atoms from the particle reducing the overall size of the original particle (see Figure A-3).

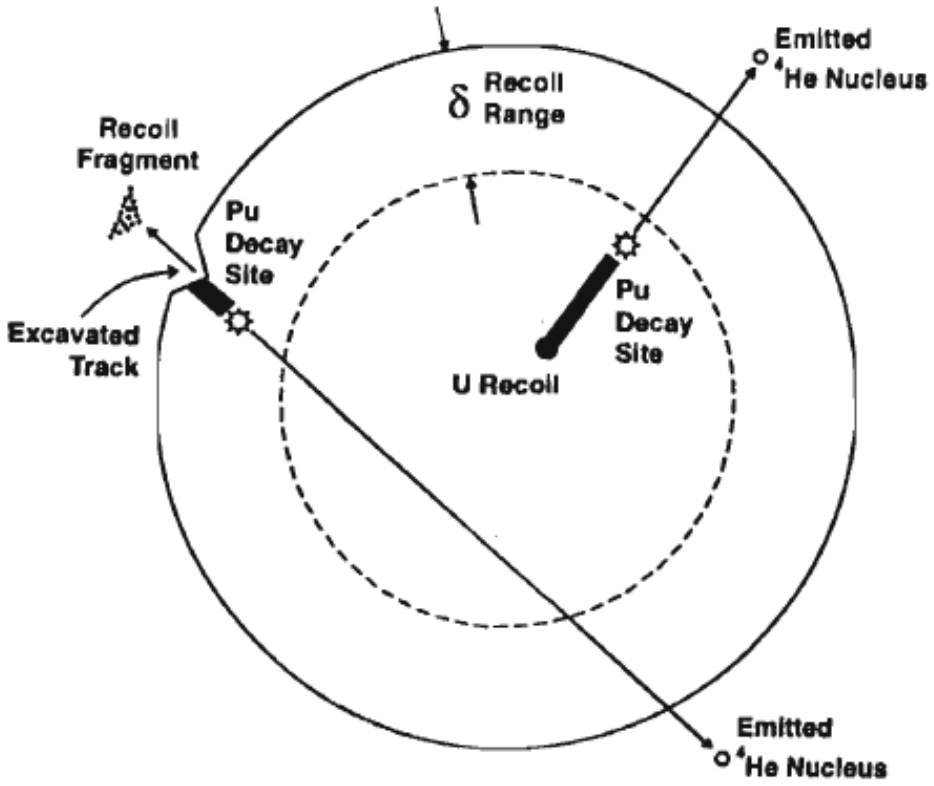

Figure A-3. Specific activity-dependent plutonium fragmentation model of Fleisher.[9]

The major structural damage is not the result of alpha decay (even though the particle carries most of the energy) but due to the residual heavy nucleus. If the atom that decays is not within the recoil range, δ, of the particle surface, the number of atoms in the particle is unchanged. If, however, the decay occurs near the surface (i.e., within δ of the surface), the recoil nucleus may be ejected and could carry with it additional atoms, reducing the overall particle size. This radiation damage model, which closely matched observations, predicted that "subparticles" of up to 10,000 atoms in size are created.

In the second model, the initial damage is created by the alpha particle, which subsequently is attacked by the water and a "multi-atom" particle is released. The average rate of particle loss with this model was about 1,000 atoms per particle.

In either case, it can be concluded that PuO_2 particles "dissolve" in water through a process of fragmentation, which is induced by alpha particle decay of the radionuclide, and that $^{238}PuO_2$ dissolve at a faster rate than $^{239}PuO_2$. This results in faster clearance by $^{238}PuO_2$ from the lung than $^{239}PuO_2$ and this fragmentation lowers the plutonium lung burden but makes more plutonium available to be deposited in other organs of the body.

A-5.3 Inhalation and Particle Size

Experience in the nuclear industry has shown that the most likely route of accidental exposure of workers is by inhalation. This route of exposure has been evaluated with regard to the absorbed radiation dose to the respiratory tract, and the respiratory tract as a portal of entry of plutonium to the blood.

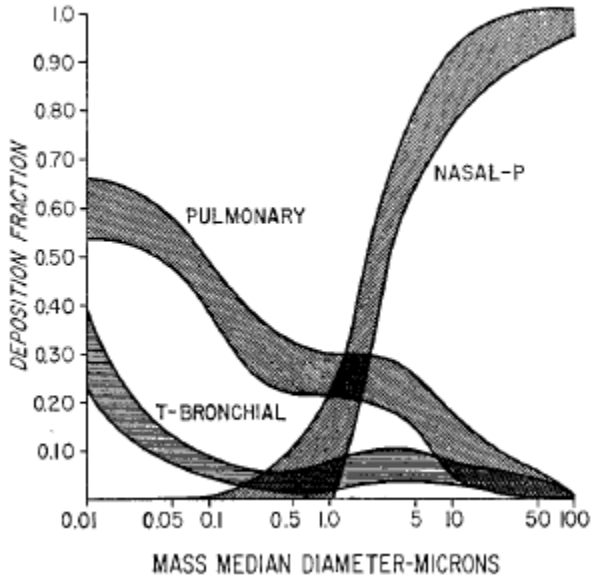

Figure A-4. Mass median diameter microns. Each of the shaded areas (envelopes) indicates the variability of deposition for a given mass median (aerodynamic) diameter in each compartment when the distribution parameter σ_g varies from 1.2 to 4.5 and the tidal volume is 1450 ml.

A-5.4 Human Health Risks

There are no direct data on health effects from Pu-238 in humans, and only limited data on Pu-239, from which one can estimate health risks. Data on the health effects of Pu-238 in experimental animals at relatively high exposure levels is used to compare the response of Pu-238 to that of Pu-239. The translocation and internal distribution of inhaled Pu-238 is attributed to radiolytic fragmentation owing to its higher specific activity. This more rapid translocation from the lung results in a reduced lung cancer risk and an increased risk of bone and liver cancer from inhalation of $^{238}PuO_2$ particles compared with $^{239}PuO_2$. One study, based on estimated cumulative doses to the lung and taking into account the tissue redistributions, suggests that lung cancer risks based on cumulative dose to the lung may still differ significantly per unit amount of radionuclide, with lower risks observed from $^{238}PuO_2$ particles compared with $^{239}PuO_2$.

All these data suggest that the health effects to be expected at sufficiently high radiation doses are increased numbers of cancers within those tissues that retain plutonium in highest concentration, i.e., lung, liver or bone, and that these effects are due to alpha particle irradiation. The National Council on Radiation Protection (NCRP) has recently reviewed the risk estimates recommended for cancer from alpha-particle-emitting radionuclides[10]), and for radiation protection purposes has adopted those recommended in BEIR IV (National Academy of Sciences/Nuclear Regulatory).[11] For plutonium isotopes, lifetime excess cancer deaths from lung cancer are estimated at 700 per 10^4 person-Gy; in bone, 300 per 10^4 person-Gy (dose averaged over the whole bone mass); and in liver, 300 per 10^4 person-Gy. These estimates are based on a linear, no-threshold risk model, whose validity for application to low-dose situations remains unclear.

These risk estimates for transuranic elements were derived by the BEIR IV Committee primarily from studies of human populations exposed to other alpha-emitting radionuclides. The lung cancer estimate is based on analysis of effects data in the miners who were occupationally exposed to radon and its progeny, using a nominal value of 0.005 Gy to cells of the bronchial epithelium per working level month. The estimate projects that most of the excess cancers occur in smokers. For bone cancer estimates, the committee used Bayesian analysis of human radium and animal transuranic and radium data. The 95 percent CI was from 80 to 1,100 bone cancer deaths per 10^4 person-Gy (dose averaged over the whole bone mass). For liver, the risk estimate was based on human thorotrast data.

The BEIR IV Committee cautioned that in applying these risk estimates to transuranic elements their origin as well as the great uncertainties associated with their calculation should be remembered. Differences in biological behavior and dose distribution of these surrogate radionuclides can result in errant risk estimates. Difficulties in using animal data arise from differences between animals and humans, including differences in histological types of cancer, different spontaneous risks, different confounders (e.g., smoking), and different life spans. Interpretation, extrapolation and modeling of epidemiologic data contribute another set of uncertainties. NCRP Reports No. 115 and No. 116[10,12] discuss other uncertainties inherent in radiation risk estimates, including dosimetry, quality of data (e.g., accuracy of medical diagnoses), choice of risk-projection model, extrapolation of risk from high dose to low dose/low rate situations, transferability of risk between different populations, effect of latency on risk, and projection of risks from the period of observation to total lifetime. Given these uncertainties, the risk estimates cited above represent an approximate central value for cancer risk from plutonium deposition in humans.

A-6. REFERENCES

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Appendix B

Baseline Process

Appendix B
Baseline Process

All operations requiring the handling of unencapsulated $^{238}PuO_2$ are performed in gloveboxes. These gloveboxes are constructed with stainless steel-lead-stainless steel sandwich-type walls and have highly polished interiors to facilitate cleaning. Glovebox windows are safety glass held in position by viton gaskets that are provided with stainless steel fire shields. The gloves consist of two layers of hypalon separated by a thin layer of neoprene and lead. Neutron attenuation is provided by hydrogenous shielding located outside the glovebox.

All processing gloveboxes are provided with inert gas, argon or helium, atmospheres. This is accomplished by either a continuous inert gas pass through (<10 ppm oxygen) or a closed loop recirculating system (<1 ppm oxygen). Gloveboxes are attached to one another via vacuum/inert-gas airlocks. Thus, if any glovebox is breached, the atmospheres of neighboring boxes are not affected.

For the purpose of description, the production of encapsulated GPHS pellets from raw feed powder may be separated into eight characterization and processing steps. These steps, each of which is described in detail below, are

Oxygen-16 Exchange

The first processing step involved heating the as-received PuO_2 feed powder in an O-16 environment to replace the O-17 and O-18 isotopes present in the feed with O-16. The feed powder produced with natural oxygen has a neutron emission rate in excess of 17,000 n/s-g ^{238}Pu,[1] primarily owing to (α,n) reactions caused by the presence of O-17 and O-18 isotopes in the normal oxygen used in calcining operations.

The exchange is accomplished by heating a platinum boat, filled with the appropriate amount of feed powder, in a furnace in an atmosphere of flowing Ar saturated with $H_2{}^{16}O$. The feed material is exchanged for 24 hours at 775°C and then heated for 1 hour at 1000°C to release stored helium. The furnaces are programmed for heating and cooling rates of 300°C/h. The Ar-$H_2{}^{16}O$ flow is maintained throughout the run and approximately 30 ml of $H_2{}^{16}O$ are used per 70 g of plutonia powder.[1]

Two gas streams are introduced into the furnaces at one end, pass through the furnace and then exit to the glovebox exhaust. The reaction gas consists of Ar passed through a bubbler containing $H_2{}^{16}O$ and then through the alumina core. Before these gases are introduced into the exchange furnace, they are purified by passing them through Lindberg Model 70 tube furnace containing titanium beds at 750°C. Valves and flowmeters are used to regulate gas flows. Alumina baffles are placed at both ends of the alumina tubes to moderate the flow of the Ar-$H_2{}^{16}O$ required.

The platinum boats used to contain the plutonia powder are made by deep drawing (no welded seams) to facilitate cleaning.

Ball Milling

The second processing step involves milling the feed powder to produce the desired particle size and powder morphology. This is, to some extent, a normalizing step to eliminate differences in surface activities from one lot of feed powder to the next. The as-received powder consists of two types of particles and has a mass-median diameter of about 2.7 μm. One type of particle is rosette-shaped, the other is lath-shaped. The lath-shaped particles have an extremely high surface activity and cause the material to shrink excessively when sintered. The results of developmental studies performed indicate that the reactivity of the feed will be adequately adjusted if the powder is milled to produce a mass-medium diameter of about 0.6 μm. This requires 40 hours in the ball-mill.

The mills operate at 27 rpm and approximately 2 pm of iron are introduced to the feed powder per hour of milling. Slight changes in precipitation conditions can effect a change in the ratio of lath-shaped to rosette-shaped particles.

Each ball-milling assembly consists of a set of rollers and hardened stainless steel jars. Each jar contains fifty-five 15.9-mm-diameter hardened steel (440 C) balls.

Slugging and Screening

The slugging and screening operations are performed to convert the ball-milled powder to granules of the size desired for hot pressing. The plutonia powder is divided into an equal number of approximately 25 g charges, depending on feed lot size. Each charge is cold pressed at 400 MPa to form a green pellet at 60% TD. The pellets are then broken and screened to size, and the <125 µm fraction is collected.

The cold pressing is performed with a double-acting cold press. The die punches are lubricated with molybdenum disulfide and no binder is added to the plutonia powder. All screens, pans, rollers, funnels, forceps, and brushes used in these operations are stainless steel.

Granule Seasoning

This is the most important prepress processing step. After the <125 µm granules are made they are thermally seasoned to form the reactive and nonreactive components of the grog-feed mixture. The majority of the green granules, 60 wt% are seasoned for 6 hours at 1100°C in flowing Ar-$H_2{}^{16}O$. The remaining granules, 40 wt%, are seasoned for 6 hours at 1600°C. Heating and cooling rates for both seasoning operations are 200°C/h. Seasoning the granules in Ar-$H_2{}^{16}O$ prevents the back exchange of the O-17 and O-18 and, in addition, frequently leads to a further reduction (5 to 10%) in the neutron emission rate.

The most important parameter in processing the feed before hot pressing is the temperature at which the reactive component of the grog mixture is seasoned. If the temperature is too low, the granules will be too reactive, leading to excessive shrinkage and crack formation when the pellet is postpress sintered. If the temperature is too high, the granules will not be reactive enough to form around the nonreactive high-fired granules to produce a homogeneous microstructure. Thus, it is imperative that the temperature profiles be determined accurately for the furnaces, and that temperature control and measurement systems be in good working order.

Die Preparation and Loading

The grog-type feed used to fabricate the GPHS fuel pellets is obtained by mixing the proper ratio of <125 µm granules seasoned at 1100°C (60 wt%) and 1600°C (40 wt%). The mixing is accomplished by putting the granules into a ball-mill jar and rolling it for 15 to 30 minutes at 27 rpm. No balls are used. The jar is charged with 153.44 g of granules. After the rolling is completed, the graphite hot pressing die is charged with 152.44 g of the granule mix.

The die assembly consists of a cylindrical insert, susceptor, locking pin, two punches and two endcaps. The pellet is formed in a hole bored through the insert and centered in the cylindrical axis. The susceptor is sized to the insert and the induction heating coil to maximize heating efficiency. The susceptor is provided with seven blackbody holes for temperature measurement with an optical pyrometer. The insert and susceptor are positioned relative to one another by means of a locking pin. Two punches are introduced into the insert, one from each end. The travel of the punches during pressing is determined by the depths of the endcaps.

All die parts are machined from AXM-grade graphite produced by POCO Graphite, Inc. This material has consistently proved to be free of flaws and sufficiently pure to preclude significant degassing. Use of this die assembly will produce a hot pressed pellet with a centerline diameter of 27.78 mm and a centerline length of 27.88 mm. Individual pellet dimensions will vary slightly depending on the tolerances obtained in machining the die and the reactivity of the plutonia feed granules. Shops routinely produce dies machined to tolerances of 0.005 to 0.012 mm.

Hot Pressing

The GPHS pellets are pressed one at a time in the hot press assembly consisting of a double-acting hydraulic system, a vacuum system and an induction-heating system consisting of a work coil powered by a motor generator. The hydraulic system powers the two main pressing servorams and three actuators. He servorams are mounted vertically and extend into the vacuum chamber containing the work coil. The actuators are used to raise and lower the vacuum can so that the die assembly may be introduced and removed. The die assembly is separated form the servorams by graphite spacers so that during pressing the die assembly is centered in the work coil.

After the die is positioned, the system is evacuated by means of a diffusion pump. Overnight evacuation results in a vacuum chamber pressure of 6.7 to 13 µPa.

After the chamber has been evacuated, the servorams, provided with water-cooled load cells, are positioned so that the blackbody holes in the susceptor are centered on the slot in the work coil. A slight preload, 517 kPa, is provided. The timer is started and the motor generator is brought on to 67.5% full power. The temperature is monitored with an optical pyrometer. When the temperature reaches 1300°C, about 4.1 minutes into the run, the programmed load cycle is initiated. When the susceptor temperature reaches 1530°C, about 6 minutes into the run, the motor generator is reduced to 50% power for the remainder of the run. The full programmed load, 11.8 kN corresponding to 19.5 MPa for GPHS pellets, is attained in 8 to 9 minutes from initiation of the load cycle, The die is held at 1530°C under full load for 15 minutes, although punch closure is typically attained in less than 10 minutes. At the end of the pressing cycle, the motor generator is turned off and the load is removed from the die assembly. The chamber is allowed to cool for about 1 hour and then the vacuum system is valved off and dry argon is introduced into the chamber to facilitate cooling. After the cooling period, the vacuum can is raised and the die assembly is removed. Typically, pressing is performed in the morning and the die is removed in the afternoon.

Postpress Sintering and Pellet Storage

After the pellet is removed from the die insert, it is stored in a graphite container for 16 hours or longer (overnight). Pellets may be stored for as long as 2 weeks before sintering with no obvious deleterious effects. After storage, the pellet is weighed and the dimensions are measured. The pellet is then sintered in flowing Ar-$H_2{}^{16}O$ for 6 hours at 1000°C, followed by 6 hours at 1527°C. Heating and cooling rates are 150°C/h.

The pellet is loaded, half-buried, in a platinum boat filled with high-fired thoria powder. After sintering, the pellet is weighed and the dimensions are remeasured. The volume and density are then calculated. The sintered pellet is then stored in the graphite container until transferred for use. During the sintering operation, the pellet dimensions will shrink by about 0.5 to 0.8%.

During hot pressing, the plutonia is reduced to a stoichiometry of about $PuO_{1.88}$. The pellet is stored overnight so that it will be reoxidized to $PuO_{2.0}$ or nearly so before the dimensioning activities. Similarly, the Ar-$H_2{}^{16}O$ gas flow is started before the furnace is turned on to ensure a stoichiometry of $PuO_{2.0}$ before the pellet is sintered. The use of Ar-$H_2{}^{16}O$ flow gas, of course, precludes back exchange of the material and subsequent increased neutron emission rates. The slow heating and cooling rates are employed to reduce the chance of thermally shocking the pellet. Sintering the pellet in a platinum boat filled with thoria powder prevents thermal stress points that can occur if the pellet comes in direct contact with the platinum.

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Appendix C

SRS Process Parameter Experience

Appendix C
SRS Process Parameter Experience

Inert and stable heat generating shapes of dense $^{238}PuO_2$ ceramics are produced for isotopic power applications by hot pressing granulated $^{238}PuO_2$. $^{238}PuO_2$ powder is produced by calcining precipitated Pu(III) oxalate.[1,2,3] Bickford, Rankin and Smith [4,5] have shown that variations in the particle size and particle dimensions of the PuO_2 powder cause wide variation in the density and microstructure of the fuel forms. Such variation can be accommodated by ball milling PuO_2 powder to the same particle size. However, this can only be done by adjusting milling time for each different calcined powder size. A more desirable approach is to produce calcined feed with reproducible size characteristics.

Preselected and constant size characteristics of PuO_2 feed powders can be obtained for any desired fabrication process by controlling precipitation parameters. Pu(III) oxalate precipitated by adding Pu(III) feed into oxalic acid produces bimodal, log-normal distributions of monoclinic lath particles and loosely bound agglomerates. These particles can be calcined to PuO_2 without disintegration and produce high surface area lath particles of the same bimodal distribution. The particle size and lath dimensions of the PuO_2 particles and their agglomerates are determined solely by the precipitation factors affecting final solubility of Pu(III) oxalate: precipitation temperature, nitric acid concentration, and plutonium and oxalate concentrations.

Work at Savannah River[3,6,7,8] and elsewhere[9-13] has shown that widely different particle morphologies and sizes can be obtained from oxalate precipitation, depending on several factors. These include the valence of the plutonium in solution, the mixing sequence of plutonium nitrate and oxalic acid solutions, and the variables affecting initial supersaturation (nucleation–rate) and final solubility (particle growth rate). Priority interest has been on the filterability of the precipitate. The production process used at Savannah River was to batch Pu (III) oxalate precipitation by adding plutonium nitrate solution into oxalic acid solution (reverse strike addition), filtration, and calcination of plutonium oxalate to plutonium oxide.[7] Fabrication processes for heat source fuels have been developed at LANL[14] and Savannah River[4,7,15] and the fuels qualified for application using $^{238}PuO_2$ produced by reverse-strike precipitation as the reference material.

The Pu-238 product and residual Np-237 were separated from aluminum, fission products, other impurities, and from each other by anion exchange processing (see Figure C-1). The resin columns were normally operated as fixed beds, but could be operated as agitated beds when needed for regeneration or replacement of resin. In the first cycle of anion exchange, neptunium and plutonium were both adjusted to the (IV) valence state in 8M nitric acid by treatment with ferrous sulfamate and hydrazine, followed by heating to 50°C. The neptunium and plutonium were absorbed on the resin column to separate them from aluminum, fission products, and other cationic impurities. After washing with 8M nitric acid for decontamination, the neptunium and plutonium were eluted with 0.35M nitric acid. In the second cycle of anion exchange, the solution was adjusted to 8M nitric acid, and neptunium and plutonium were again both adjusted to the (IV) valence state and absorbed on the resin. After washing with 8M nitric acid for further decontamination, the plutonium was separated from the neptunium by washing the column with 5.5M nitric acid containing ferrous sulfanate and hydrazine to reduce the plutonium to the (III) valence state. The neptunium was then eluted with 0.35M nitric acid. The separated neptunium and plutonium were processed by one or more additional cycles of anion exchange. Additional purification occurred during the oxalate precipitation.

PuO_2 powder with reproducible particle size and morphology can be produced by controlling precipitation variables affecting the initial supersaturation and final solubility of plutonium oxalate. Such feed powders with constant characteristics are essential for reproducible fabrication response and controlled microstructures in the manufacture of $^{238}PuO_2$ heat sources.

Calcination does not change the morphology or shape of the size distribution of the PuO_2 particles from that of the precipitated Pu(III) hydrated oxalate. For a given precipitation method, the size and morphology of the Pu(III) oxalate are determined by precipitation temperature, nitric acid concentration, plutonium concentration, and oxalate ion concentration. Functional relationships of these variables were developed to control and predetermine the size, extent of agglomeration, and dimensions of the PuO_2 particles over the range of these variables for PuO_2 production.

$^{238}PuO_2$ is produced by reverse-strike precipitation of Pu(III) oxalate. This technique was selected for the smaller losses of $^{238}PuO_2$ because of the lower solubility of Pu(III) as compared to Pu(IV) oxalate and for good filterability of the Pu(III) oxalate precipitate.

Pu(IV) was reduced to Pu(III) with 0.05 mole excess ascorbic acid and stabilized from reoxidation with 0.05M hydrazine. Plutonium nitrate solution was added into 0.9M oxalic acid solution, so-called reverse strike precipitation.[7] The excess oxalic acid concentration in the slurry after precipitation was 0.2M.

Reactants were mixed by a paddle stirrer rotating at ~500 rpm in a small metal precipitator with four equally spaced baffles. Reactants were added at a constant rate over a period of 12 minutes. Precipitants developed promptly, permitting filtration within 5 minutes after addition of plutonium nitrate was completed. Plutonium oxalate precipitates were calcined in air at 735°C for 2 hours. Calcined $^{238}PuO_2$ contained typically 3,000 ppm total of Th, Np, U, and Am; 150 ppm each of Ca, Fe, and Si; 20 to 50 ppm each of Al, Ni, and Cr, and <10 ppm of other cations.

$Pu_2(C_2O_4)_3 \bullet 10H_2O$ crystals precipitate as monoclinic laths isomorphous with crystals of La(III) and Ce(III) oxalates investigated optically by Wylie.[17] The lath crystals exhibit anisotropic growth along the principal axes with growth rate ratios observed at high precipitation temperatures (large laths) parallel to the [001] face and perpendicular to the [001] direction, indicative of rapid and pulsating growth in the Z direction.

Very little crystal branching was observed. This indicates that the rate-limiting step is the intrinsic growth rate of the oxalate crystals, and not the diffusion of solute to the crystal.[20] The behavior is consistent with the large super-saturation and the large entropy of precipitation. (The ratio of plutonium concentration in the feed to that in the final slurry varied between 50 and 1,500 for the range of variables in this work based on solubilities measured by Burney and Porter).[19] The absence of dendritic growth and the rate-limiting step of intrinsic crystal growth are the principal reasons that predetermined, uniform, and reproducible powder size and morphology can be obtained by controlling only the precipitation variables.

Morphology of the particles and the shape of the size distribution are preserved on calcination even though large molar ratios of H_2O, CO_2, and CO are evolved from the crystals. Conversion to PuO_2 without disintegration is attributed to the escape of water preferentially along (100) planes in the crystal.[19] About a one-third linear shrinkage occurs in calcination to PuO_2 at 735°C as determined from particle size measurements.

Particle Size Distribution

Typical mass particle size distributions of calcined PuO_2 are shown in Figure C-2. Parameter effects are shown in Figures C-3 and C-4. The log normal statistics suggest no decrepitation on calcining or fracture on stirring. The size distributions of both plutonium oxalate and PuO_2 are usually bimodal, representing a distribution of individual lath particles and a distribution of agglomerates of laths.

Both surface area and crystallite size PuO_2 within the particles are a strong function of calcining temperature.[6] The relatively high surface area and its strong inverse temperature dependence are associated with fine porosity generated within the particles by escaping H_2O, CO_2, and CO during calcining. Surface area and crystallite size are both largely independent of particle size morphology. See Figure C-5.

Experiments showed that particle size could be predetermined by controlling precipitation temperature, nitric acid concentration, plutonium concentration, and oxalic acid concentration. The particle size of PuO_2 increases with the temperature of the precipitation slurry in an Arrhenius relation. All three dimensions of the laths increase with precipitation temperature. PuO_2 particle size increases with increasing nitric acid concentration in the plutonium feed solution. Particle size decreases with increasing plutonium concentration above room temperature, but is rather insensitive to plutonium concentration at room temperature. Particle size decreased with increasing oxalate concentration.

The production precipitator at Savannah River Site was originally intended for producing fine powders and was not optimized for specific particle size distributions. An ideal precipitator would control nucleation and growth of particle through several design features. First, the agitation would be sufficient to disperse and suspend particles, without shearing them to create new nucleation sites. Further, a smooth inner surface without heals, and an efficient flushing mechanism would avoid nuclei from previous batches. Temperature control of the reagents and precipitator would also improve uniformity. The HB-Line precipitator was limited by the fluctuating temperature of the chilled water system. Reagent addition rates must also be controlled.

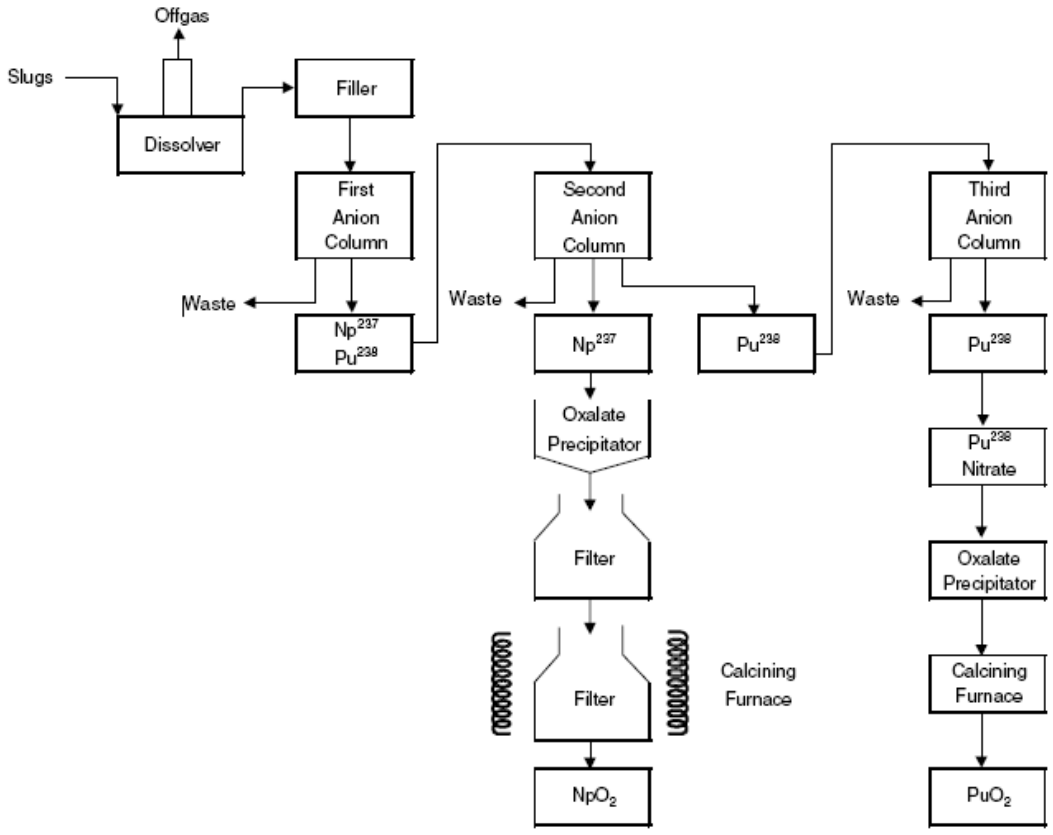

Figure C-1. SRS HB line production steps for Pu-238 purification.

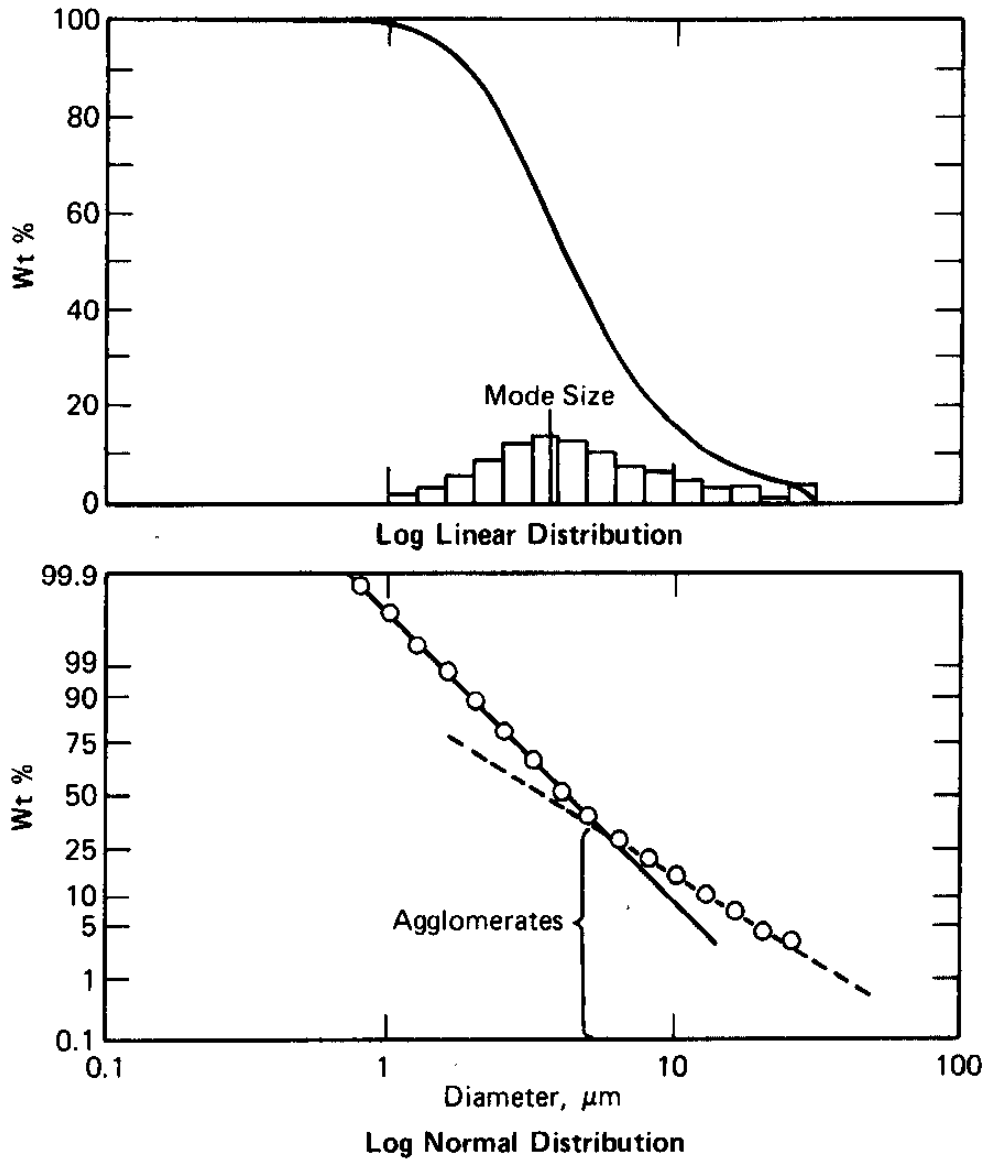

Figure C-2. Mass particle size distribution of PuO_2.

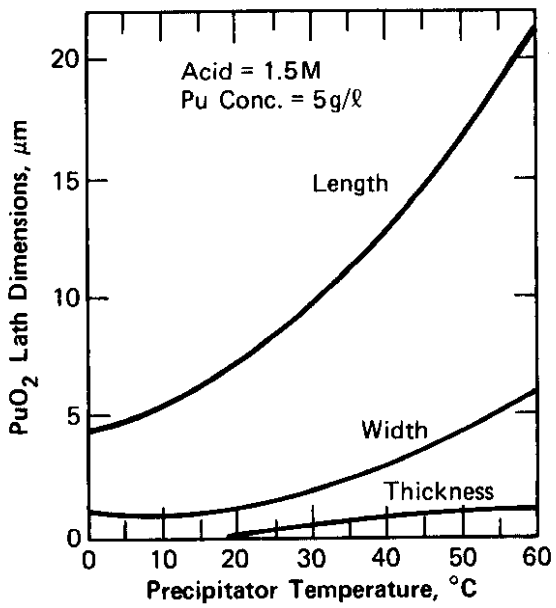

Figure C-3. Effect of temperature on PuO_2 lath dimensions.

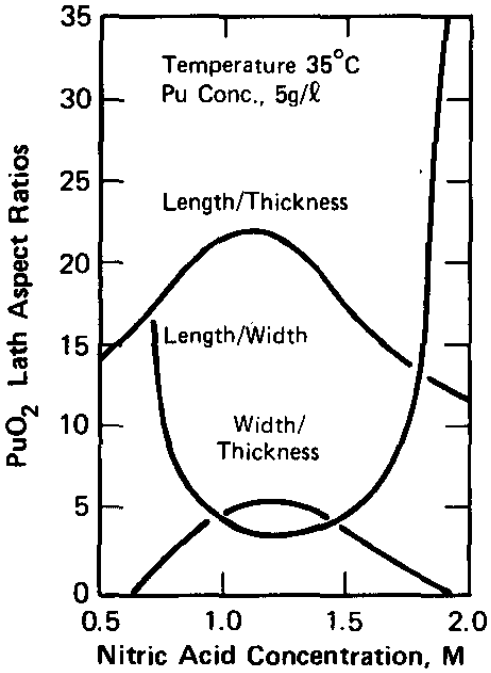

Figure C-4. Effect of nitric acid concentration in precipitation feed on the ratios of PuO_2 crystal dimensions.

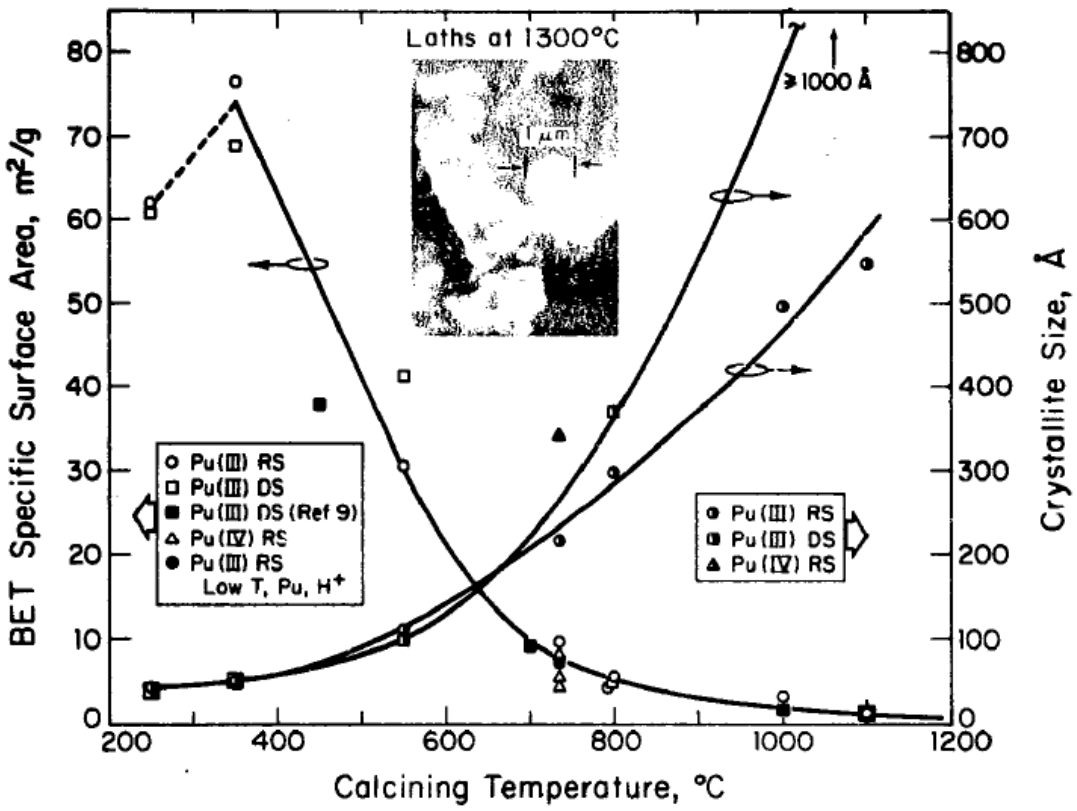

Figure C-5. Specific surface area and crystallite size of PuO_2 versus calcining temperature and oxalate precipitation technique.

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Appendix D

Pellet Fabrication

Appendix D1
Liquid Phase Sintering

D-1. LIQUID PHASE SINTERING

D-1.1 Microstructure of GHPS Pellets

A typical microstructure of a GHPS pellet after the final postpress sintering treatment at 1527ºC is shown in Figure D1-1. Porosity is of two types—intergranular and intragranular. Here, intergranular and intragranular refer to the original granules and not to grains. From Figure D1-1 and other micrographs found in reports on the subject, it has been observed that most intergranular pores appear to be closed. Most are small pores inside grains that appear to have been trapped during grain growth, and, therefore, are not connected to a porosity network. The importance of this observation is that the 1100ºC sintered granules (60%) do not appear to contribute significant open porosity and can be eliminated as long as another method of bonding between 1600ºC granules (40%) is found.

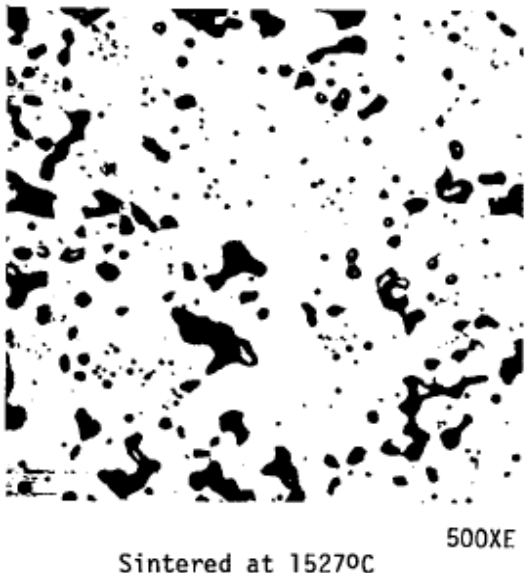

Figure D1-1. Microstructure of postpress sintered GHPS pellet (final pellet, ready for use).[1]

Microstructures in which high fractions of liquid phase are present are easily discernable from rounded grains in the microstructure. Figure D1-2 shows an example of UO_2 rounded grains in Depleted Uranium Aggregate (DUAGG™) used in heavy cement for shielding.

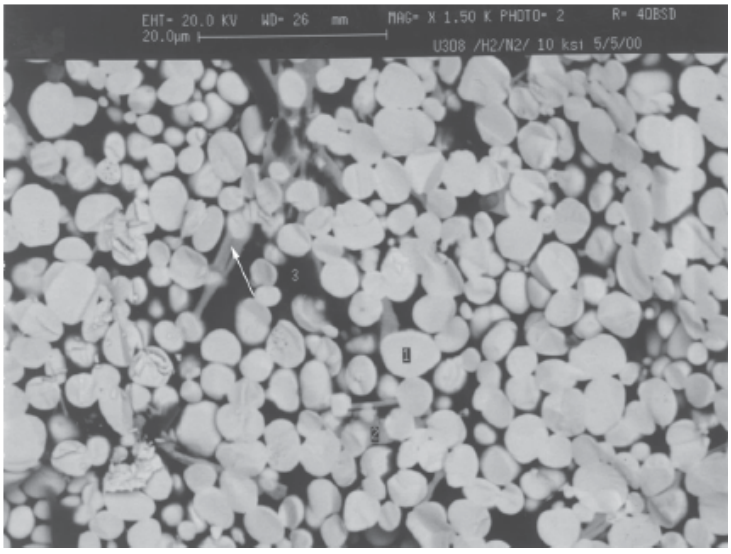

Figure D1-2. Microstructure Depleted Uranium Aggretate granules used in high density radiation shielding cement. UO_2 grains are rounded owing to mineral additions that form the liquid phase.

D-1.1.1 Granule Packing

Discrete distributions of coarse and fine particles can be mixed so that the fine particles occupy the interstices between the coarse particles. Coarse spherical particles must be at least a factor of seven larger than the fine spheres to fit in the interstices, as noted in Section 5.3.4. McGeary packed steel spheres 95% dense by using four levels of increasingly smaller spheres. In practice, however, mixtures of coarse and fine nonspherical powders in the size range of the granules used in the GHPS pellets seldom reach above 70% unless a very wide size range is used.

D-1.1.2 Liquid Phase Additives

The $PuCl_3$-rich end of the phase diagram for $PuCl_3PuOCl$ is shown in Figure D1-3. Over the compositions covered in the phase diagram, a liquid phase exists above 747ºC. Information is not available regarding the wetting or solubility of the liquid compositions with PuO_2. As an alternative, PuF_3 may be used for the liquid phase. It melts at 1425ºC and is one form of a reprocessed plutonium.

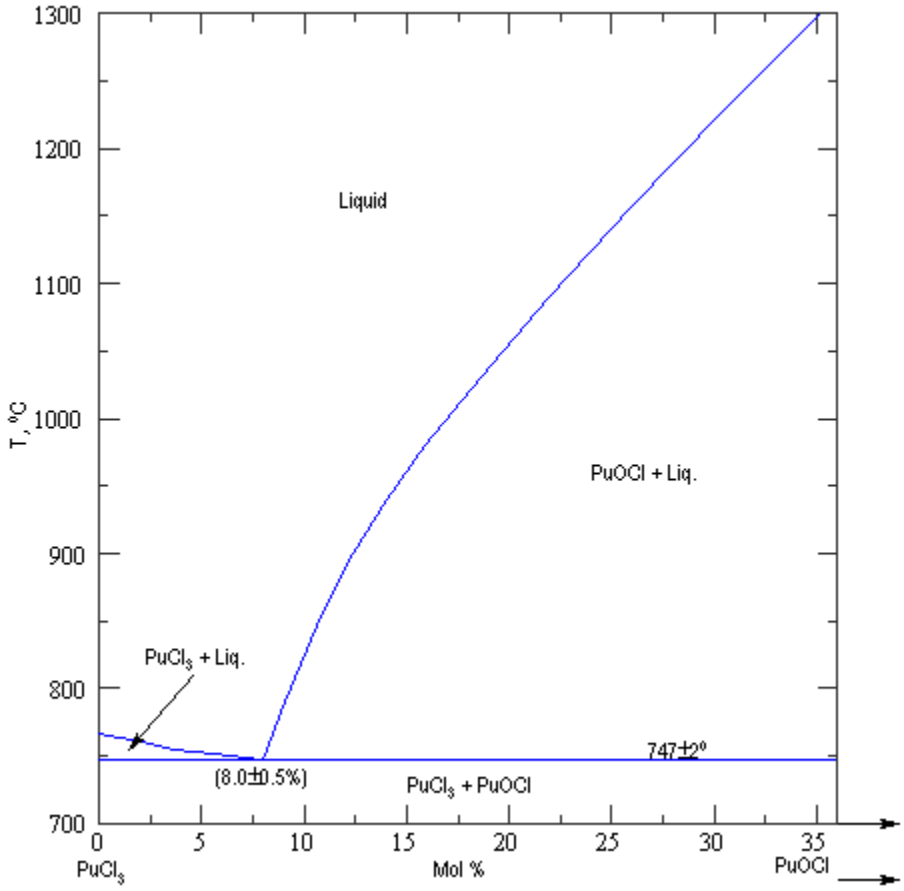

Figure D1-3. Phase equilibrium diagram for the $PuCl_3$-PuOCl system.[3]

D-1.1.3 References

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Appendix D2
Reaction Bonded Plutonium Oxide

D2-1. REACTION BONDED PLUTONIUM OXIDE

This appendix contains some details of the reaction bonded process that was summarized in Section 5.3.3. The suggested process for making RBPO has not yet been attempted. Reaction bonded aluminum oxide is discussed below for comparison of processes and properties.

D2-1.1 Calculation of Final Density After Reaction Bonding Comparing Al_2O_3 and PuO_2

The following is an example of a calculation of how much sub-oxide (rather than Pu metal) would be necessary for reaction bonding. It is for illustration only, because it is not known which sub-oxide will form and what the theoretical density of that sub-oxide would be. For the calculation, Pu_2O_3 is assumed to be the sub-oxide. The relative final density, ρ_{rf}, for reaction bonding of a specific ceramic is exactly determined by the relative initial (green) density, ρ_{ri}, the fraction of metal oxidized during reaction bonding, *f*, (after reaction bonding at a sufficiently high temperature this will be approximately 1.0), and the fraction of metal powder, $V_{M,}$ according to the equation,

$$\rho_{rf} = \frac{\rho_{ri}\rho_M M_{MO} f V_M X_{MO} + \rho_{ri}\left(1 - V_M\right)\rho_{MO} M_M}{M_M \rho_{MO}}$$

ρ_M is the theoretical density of the metal or sub-oxide. $\rho_{Al} = 2.71\, g/cm^3$; $\rho_{Pu} = 19.84 g/cm^3$

The theoretical density of β-Pu_2O_3, which has a hexagonal structure, is estimated from lattice parameter data of Gardner et al[1] $\rho_{Pu_2O_3} = 35 g/cm^3 \left(Appears\ too\ high\right)$

M_M is the metal or molecular weight of the sub-oxide. $M_{Al} = 26.98 g/mole$;
$M_{Pu_2O_3} = 538 g/mol.wt.$

ρ_{MO} is the theoretical density of the oxide. $\rho_{Al_2O_3} = 3.96 g/cm^3$; $\rho_{PuO_2} = 11.46 g/cm^3$

M_{MO} is the molecular weight of the oxide. $M_{Al_2O_3} = 102 g/mole$; $M_{PuO_2} = 276 g/mole$

X_{MO} is (number of cations in the sub-oxide molecule (or one for metals) divided by number of cations in one molecule of oxide) $X_{Al_2O_3} = 0.5$; $X_{PuO_2} = 2.0$

Example calculations: Assume $\rho_{ri} = 0.65$ and $f = 1.0$ for both cases

RBAO

Assume a typical value for Al metal additions: $V_M = 0.6$ then $\rho_{rf} = 0.76$ or 76% dense

RBPO

Assume $V_M = 0.15$ then $\rho_{rf} = 0.85$ or 85%. *V_M=0.15* translates to a 1.4 μm thick layer of Pu_2O_3 on a 50 μm diameter PuO_2 granule.

D2-1.2 Description of the Reaction Bonded Al_2O_3 Process

In the RBAO process, Al and Al_2O_3 powder are attritor milled together in an organic solvent for up to 24 hours. During milling, Al particles partially oxidize. Table D2-1 from Bertrand et al[2] lists different milling conditions, along with the compositions used in their study, and presents the analyzed oxygen content resulting from milling. Note that oxidation of between 6% and 49% occurs during milling depending on composition and milling conditions. Parts are then cold pressed in preparation for subjecting them to a heating schedule under flowing air. At approximately 500ºC, the green Al/Al_2O_3 part begins to rapidly oxidize. The outer surface of the part oxidizes first and provides a semi-rigid skeleton. If oxidation is too rapid, the part will crack at this stage, so the heating schedule is slowed down. Some investigators note that it is preferable for kinetic and microstructural reasons to achieve most of the oxidation below 500ºC.[3,4] Even under slow, controlled heating, the part expands as indicated by Figure D2-1 from Bertand et al.[2] For high strength applications, it is important that ~70% of the oxidation take place below the melting point (660ºC), but for permeable membrane applications most of the oxidation is above the melting point.

From Figure D2-1, it is noted that as much as 4% expansion was observed under some conditions, which is followed by contraction caused by sintering. Sintering is not anticipated in the proposed process.

Table D2-1. Milling conditions of reaction bonded aluminum oxide.[2]

Powder mixtures

Batch	Composition (vol.%)	Mean size (μm)	Milling time (h)	Amount of Al oxidised (vol.%)	d_{50} (μm)
#1	Al_C (40)–Al_2O_3 (60)	1.2	–	6	1.2
#2	Al_C (40)–Al_2O_3 (60)	1.2	24	31	0.3
#3	Al_C (80)–Al_2O_3 (20)	1.5	8	12	0.5
#4	Al_E (60)–Al_2O_3 (40)	3.1	8	49	0.9
#5	Al_E (80)–Al_2O_3 (20)	3.9	8	8	1.8
#6	Al_E (80)–Al_2O_3 (20)	3.9	28	26	0.9

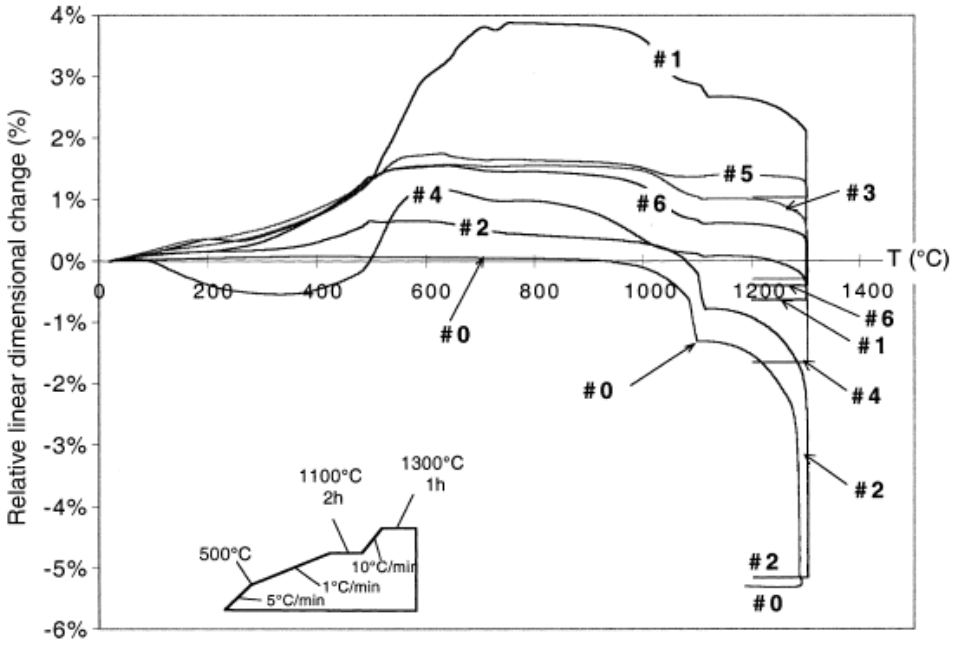

Figure D2-1. Expansion noted during some reaction bonded aluminum oxide sintering experiments.[5]

D2-1.3 Strength of Reaction Bonded Ceramics

Several investigators have measured high-fracture strengths of RBAO. Bertand et al,[2] for instance, measured the fracture strength of their RBAO to be consistently higher than that of sintered alumina containing the same amount of porosity (see Figure D2-2). They suggested that the low grain boundary energy results from impurities in the metal that increased the fracture energy. Because fracture strength is proportional to the square root of fracture energy, γ_f and fracture energy for intergranular fracture is $\gamma_f = 2\gamma_s - \gamma_{gb}$ where γ_s is the surface energy and γ_{gb} is the grain boundary energy, then a lower γ_{gb} leads to a higher fracture strength. Whether this explanation is correct or not, experimental results show RBAO, as well as reaction bonded silicon nitride, are very strong. It is plausible to think, especially in the proposed RBPO process, that sub-oxide powders oxidize and grow into the crevices of neighboring granules, making a strong bond. In contrast, sintering of powder packed onto the granule will shrink away from the granules, which possibly will leave microcracks.

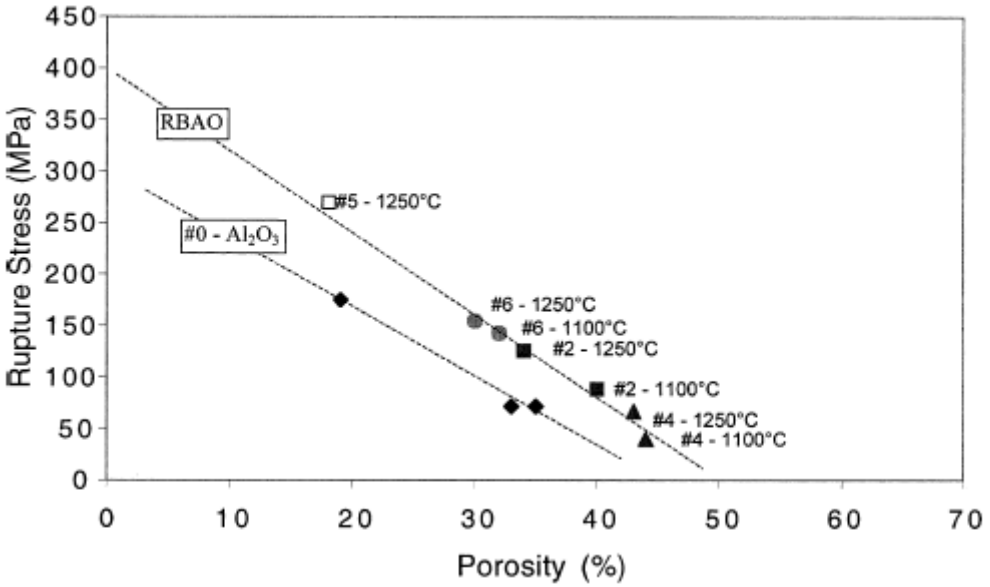

Figure D2-2. Rupture strength versus porosity for reaction bonded aluminum oxide-processed ceramics.[5]

D2-1.4 Kinetics: Control of the Oxidation Rate

The two reasons why a controlled slow rate of oxidation is necessary are (1) rapid expansion from oxidation causes nonuniform stresses and cracking and (2) oxidation is highly exothermic and can run away if the heating rate is too fast. To avoid too rapid heating, feedback system controls, which are commercially available, can be used either by in situ thermogravimetric control[3] or more commonly by oxygen demand (or in the case of reaction bonded silicon nitride, by nitrogen demand).

According to Suvaci et al,[4] the rate of oxidation of RBAO is controlled by Knudsen diffusion of oxygen through the pores to the interior of the sample. They claim this limits the size of the part to approximately 7 mm in thickness. Knusen diffusivity is directly proportional to the pore size. Suvaci et al,[3] estimated the pore size of RBAO at less then 50 nm in diameter. In the proposed RBPO process, the maximum dimension of the relevant intergranular pores will be on the order of microns, at least 20 times larger. GPHS pellet size is 28 mm, only a factor of four larger than the 7 mm thickness, so the size should be acceptable from a diffusion point of view. But from an exothermic heat point of view, a slower heating rate will be necessary because of the size.

An important difference to be dealt with in the proposed RBPO process is the self heating of the GPHS pellet. Temperature control will be difficult and so controlled oxygen feed will be important.

D2-1.5 References

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2. Bertrand, S. et al, "Processing, Microstructure and Mechanical Strength of Reaction-bonded Al_2O_3 Ceramics," *Ceramics International*, Vol. 29, No. 7, 2003, pp. 735-744.

3. Suvaci, E.; Simkovich, G.; Messing, G. L., "Reaction-bonded Aluminum Oxide Process: I, the Effect of Attrition Milling on the Solid-State Oxidation of Aluminum Powder," *Journal of American Ceramics Society,* Vol. 83, No. 2, 2000, pp. 299-305.

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5. Watson, M. J.; Chan, H. M.; Harmer, M. P.; Caram, H. S., "Feedback-controlled Firing of Reaction-bonded Aluminum Oxide," *Journal of American Ceramics Society,* Vol. 88, No. 12, 2005, pp. 3380-3387.

Appendix D3
Preforming and Pressureless Sintering

D3-1. PRESSING TECHNIQUES

Binders and lubricants are frequently used in green pressing. Problems associated with their use in preforming $^{238}PuO_2$ derive from the radiation and heat generated by $^{238}PuO_2$ that over time will tend to damage or destroy the function of most organic additives.

It must be noted that a number of ceramic materials are green-pressed (or otherwise formed) without the use of organic additives. If the shape of ceramic particles is controlled, they can be pressed to provide sufficient interlocking and binding forces. Then additives are not needed. In addition, inorganic additives (such as various clays) are often used to produce many ceramic parts.

Ceramic pellets containing AmO_2 have recently been produced by the French without using any binders.[1] No organic binder was used because of radiation damage from the AmO_2. However, a special three-piece metal die was designed and built to uniaxially press pellets (double-acting press). (See Figure D3-6.) Presumably, the die was found necessary to allow ejection of green pellets (without organic binder) without cracking as shown in Figure D3-7. The special three-part die would be very difficult to automate. Dry-bag isostatic pressing has been automated by the automotive industry (see Figure D3-5). Good release of parts from the polyurethane walls of the dry-bag isostatic press is usually achieved. If not, lubricants can be applied to just the walls (not inside the powder) before pressing.

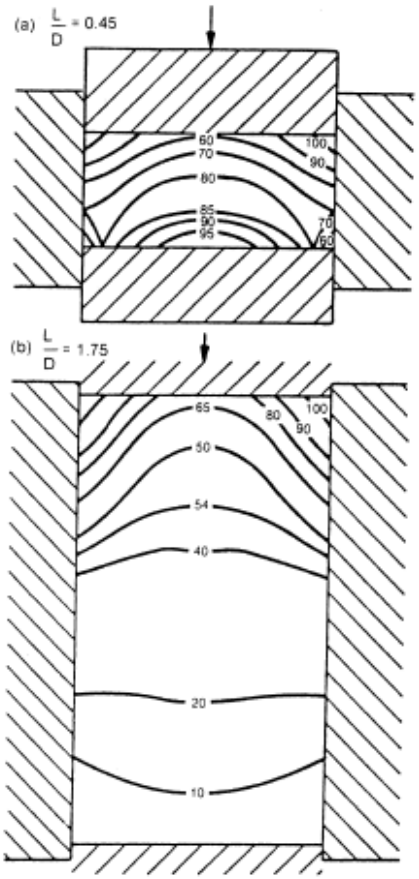

Figure D3-1. Pressure variations in uniaxial pressing owing to die-wall friction and particle-particle friction. This leads to nonuniform density of the pressed compact that is greatly enhanced as the pellet becomes taller (L/D ratio increases).[5]

Traditionally, fabrication of MOX pellets has used binders/pore formers such as AZB (azobenzone or azodicarboxamide). However, commonly used pore formers and lubricants have melting points between 100 and 200°C. Any large $^{238}PuO_2$ pellet will exceed these temperatures. Cellulose is a little better, with melting points between 220 and 260°C. However, there is the possibility of using organic binders/pore formers that convert into "char" when they are heated in an inert atmosphere and therefore retain mechanical strength and adhesion. Later, these binders can be burned out as part of sintering in an oxygen-containing atmosphere. Examples of these binders are furfural (furan-2-carbaldehyde = $C_5H_4O_2$) and phenolic resins. Phenolic resin can include any of various synthetic thermosetting resins, obtained by the reaction of phenols with simple aldehydes (e.g., phenol formaldehyde) and used to make extremely tough and strong molded parts ("Bakelite"), coatings and adhesives. Furfural, and its derivative furfuryl alcohol, can be used either by themselves or together with phenol, acetone, or urea to make solid resins. Such resins are charred in place to form carbon for automotive brake pads. Using these binders can also be helpful in creating large residual pores in ceramics. Residual carbon (e.g., cellulose-derived) has been used to produce controlled porosity in MOX fuel to be irradiated to high burnup in fast breeder reactors.[2]

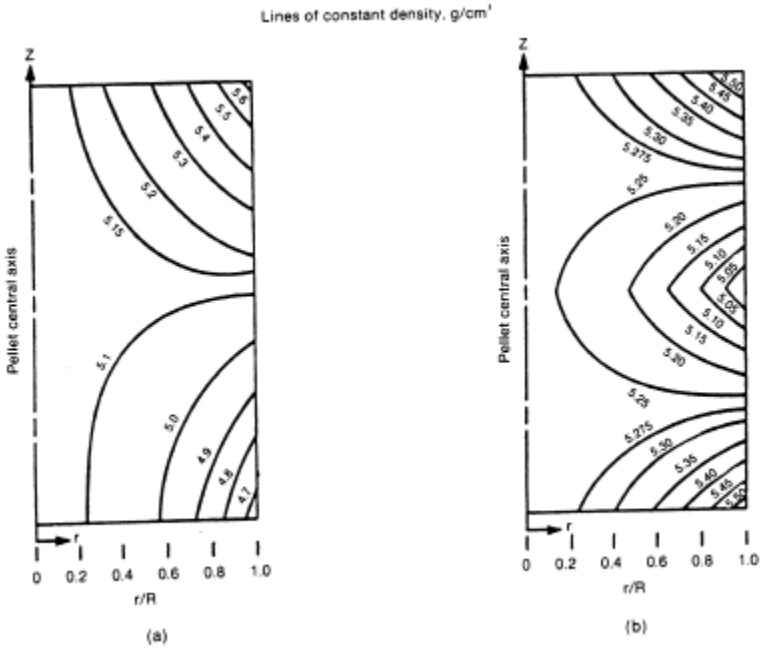

Figure D3-2. Decrease in pressure curves and increase in uniformity of density by use of double-acting press (right –b) versus single-acting press (left-a).[5]

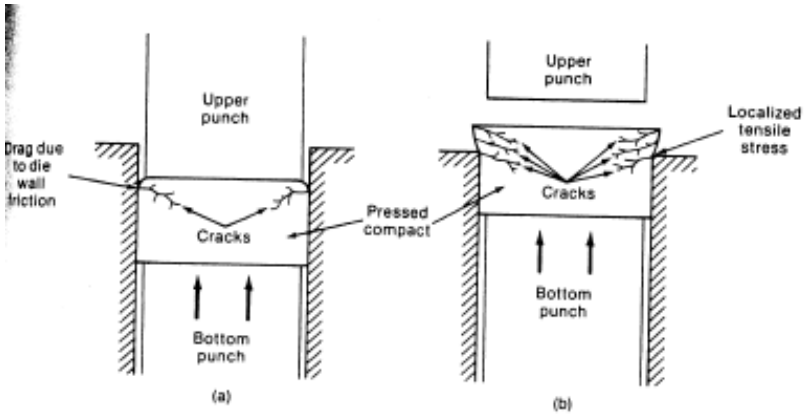

Figure D3-3. Formation of laminar cracks in pressed parts as (a) pressure is relieved from upper punch and (b) material rebound at top of die.[5]

It also seems possible to develop "sticky" inorganic binders resistant to heat and radiation that "set" like a cement when heated. An example would be adding a small amount of very fine UO_3 or UO_2 that is hydrated into a gel. The benefit would be that the gel plus associated water would act as a lubricant and binder during green pressing. The internal radiation field and heat would vaporize the free water and set the gel to act as a binder. This new idea would use of one or more of a series of uranium (or possibly plutonium) inorganic compounds as a lubricant/binder additive for pressing powders into nuclear fuel pellets. The proposed inorganic additive is one of the uranium oxy-hydroxide minerals that form hydrated gels. This mineral gel could be added in a small amount (e.g., 1-5%). Examples of this mineral gel include Schoepite $[(UO_2)_8\ O_2(OH)_{12}](H_2O)_{12}$ and hydrated $UO_3 \bullet 2\ H_2O$. Previous experience at INL in grinding UO_3 in water with an attrition mill demonstrated that a very sticky hydrated gel ($UO_3 \bullet H_2O$) could be formed in less than 1 hour. Schoepite consists of neutral $[(UO_2)_8\ O_2\ (OH)_{12}]$ sheets that are hydrogen-bonded to each other through interstitial H_2O groups. The sheets are interleaved with interlayer H_2O groups. Therefore, this structure lends itself to lubricity. The Schoepite will be dehydrated irreversibly by drying at about 120°C into a defect structure-derivative of alpha-$UO_2\ (OH)_2$ with a composition of $UO_3 \bullet 0.75H_2O$. The dehydrated Schoepite material will be crystalline with some strength and should allow for sintering of $^{238}PuO_2$ in air or oxygen. Similar inorganic compounds exist for Pu as noted in Section 5.3.2 and Pu-239 could be used.

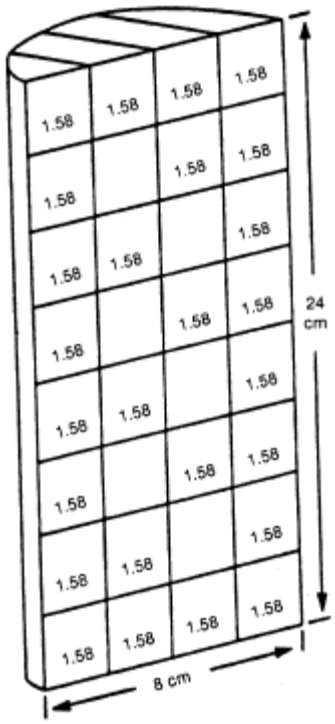

Figure D3-4. Uniform density is achieved in a solid cylinder by isostatic pressing.[5]

Historically, solid state sintering has used powders with fine, active particles (crystallites) with median diameters in about the 0.3 μm to 3 μm range. Sintering these powders at high temperatures often results in pellets of high (>95% TD) density with evenly distributed porosity. One of the earliest documented use of slugging of fine powders to prepare thermally stable UO_2 fuel pellets (larger amounts of stable porosity) was by Pope and Radford.[3] This procedure was precompacting (called "slugging") of green granules to a high density and then adding finer granules and pressing the mixture to a lower pressure/density and sintering at high temperatures. The procedure leads to high-density areas (agglomerates or aggregates) remaining from the slug in which preferential sintering has occurred being partially surrounded by low-density regions of large size porosity (often referred to as a "skeletal" structure. The same slugging procedure has been used to produce $^{238}PuO_2$ granules. The LANL process sinters 60% of the granules to 1100°C, and 40% at 1600°C. The 1600°C granules are highly dense and have lost their activity or driving force for sintering, and are considered "hard" granules. GPHS pellets are then fabricated (densified) by hot pressing this mixture of granules. However, using fine particles (derived from ball-milling) of $^{238}PuO_2$ has caused glovebox contamination problems. This is especially true for the manual slugging and screening process used to produce green granules.

To reduce glovebox contamination from fine powders, it will be necessary to replace the slugging method with other methods to produce granules (soft/lightly bonded crystallites, or hard/highly bonded crystallites). Alternate methods to produce different types of granules are covered in Sections 5.1 and 5.2.

The fabrication technology to produce low density (80-88% TD) fuel pellets from recycled (crushed and ground sintered-pellets) has been addressed in an initial study by the Japanese of Japan Atomic Energy Agency.[4] To fabricate low-density pellets for the fast breeder reactor, Japanese of Japan Atomic Energy Agency selected the method of using organic additives as pore formers in MOX powder. However, the high levels of pore-former addition caused greater deviations of sintered pellet densities, because their pore formers distributed unevenly in the MOX powder owing to the difference of bulk density between pore former and MOX powder. Low yields lead to an increased amount of scrap pellets. Therefore, experiments were conducted to use a combination of a lower amount of organic binder (e.g., 2%) and pore former (e.g., cellulose) and a mixture of hard granule sizes (fine = <10 μm, 1m^2/g, medium-coarse = <100 μm, 0.5m^2/g, and coarse = <250 μm, 0.1-0.2m^2/g) ground from MOX pellets. As little as 25% fine granules could produce the desired porosity for MOX (86-88% TD). These experiments have relevance to mixing of granule sizes for sintering $^{238}PuO_2$ pellets.

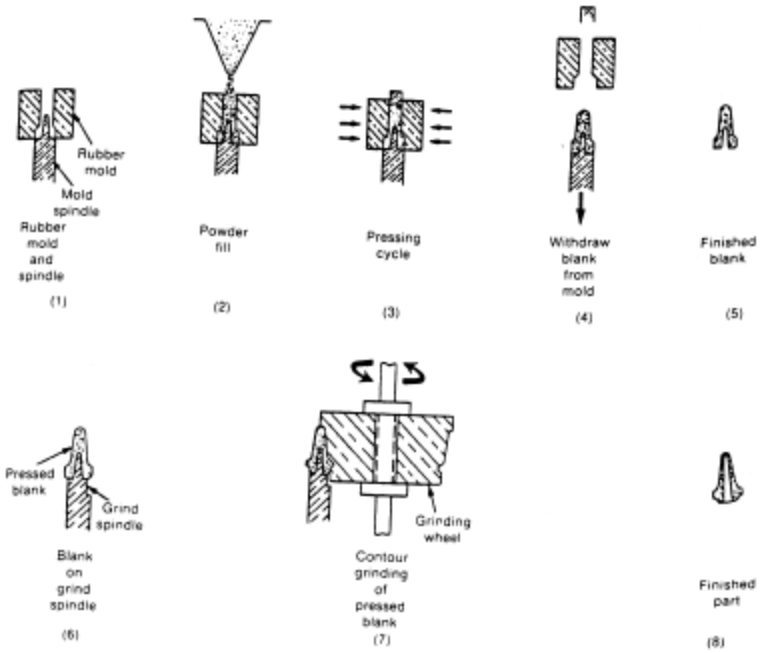

Figure D3-5. Automated dry-bag isostatic pressing and profile-grinding of a zirconia oxygen sensor electrolyte.[5]

Figure D3-6. Specially designed three-part metal die used by the French (CEA, Bagnols-sur-Ceze Cedex, France) to produce AmO_2-containing material (left) without binder. Resulting sintered pellet is shown (at right).

Selecting proper weight fractions for mixing various granule sizes can lead to optimized packing (high green density). This is illustrated in Figure D3-8 for the practical case of tabular alumina. Computer programs can also calculate packing formulas to minimize green porosity (maximize green densities) for various granule size distributions.

When using sintered (hard) granules, it is important to select granule sizes so that they pack to a high tap density. These granules could then be green-pressed (e.g., dry-bag isostatic press) to achieve even higher green density. A practical value for these green densities might be in the 70% TD range. When pressed, adjacent sintered granules will touch, so there will not be much shrinkage during sintering (e.g., to 82-86% TD). This process will achieve better dimensional tolerances on the final sintered part.

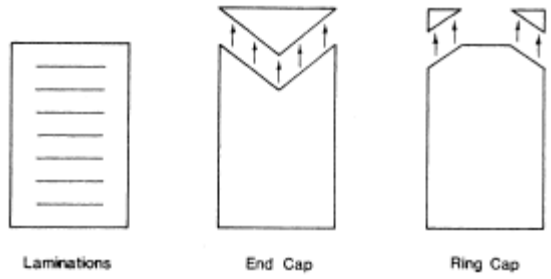

Figure D3-7. Defects that can be found in green-pressed pellets with large L/D ratios.

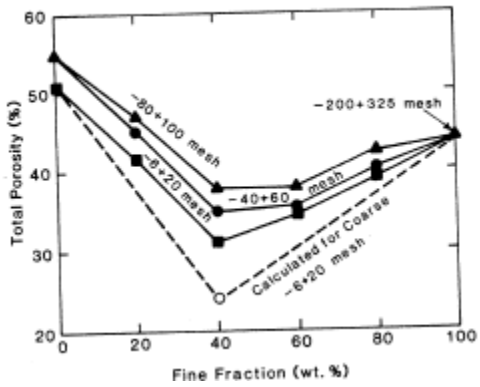

Figure D3-8. Experimental and calculated total porosity for packing of different size tabular alumina particles. Tabular alumina particles have internal porosity.[6]

D3-1.1 Pressing Technique References

1. F. Jorion et al, "The Futurix-FTA Experiment in Phenix: Status of Oxides Fuels Fabrication," *Global 2007, Boise, Idaho, Sept. 9-13, 2007*.
2. K. Asakura and K. Takeuchi, "Effect of Residual Carbon on the Sintering Behavior of MOX Pellets," *Journal of Nuclear Materials*, Vol. 348, 2006, pp. 165-173.
3. J. M. Pope and K. C. Radford, "Stable Reactor Fuel of Controlled Density Using Active UO_2 Powders," *Materials Research Bulletin*, Pergamon Press, 1976, Vol. 11, pp. 585-592.
4. T. Murakami, K. Zuzuki, and S. Aono, "Study on Characteristics of Recycled MOX Powder Suitable for Low Density Pellet Fabrication," *Global 2007, Boise, Idaho, Sept. 9-13, 2007,* pg. 891.
5. David W. Richerson, *Modern Ceramic Engineering*, Second Edition, Marcel Dekker, Inc., 1992.
6. James S. Reed, *Principles of Ceramics Processing*, Second Edition, Wiley-Interscience, 1995.

D3-2. COLD-PRESS AND SINTER DISCUSSION

The standard technique the nuclear industry uses to fabricate millions of UO_2 and MOX fuel pellets per year is to cold (room temperature) press to a green shape, then sinter (densify) at 1600°C to 1650°C for 4 to 6 hours. This technique has been studied and enhanced to produce an excellent, consistent product, but only a few dozen GPHS pellets are required for each mission and batch quantities are small, so the manufacturer is not able to run extensive process parameter characterization tests. However, the basic pressing and sintering behavior characteristics of PuO_2 are now fairly well understood and can be used to guide manufacturing of ^{238}Pu GPHS pellets.

In 1976, the Savannah River Laboratory ran a cold press and sinter test using ^{238}Pu oxide material.[1] The pellets were pressed at 58,000 psi without a binder or additive. Some pellets were fabricated from as-calcined powder and some with powder that was milled to increase ceramic activity and subsequently the fines content. Figure D3-9, copied from the report, presents two curves showing a typical relationship between sintering temperature and resulting density. Finely milled PuO_2 powder will normally sinter to ~95% TD at 1600°C or above. The dashed line shows the density reached at each temperature with the PuO_2 powder that had been calcined but not milled. The results were pellets that reached densities about 5% TD lower than the milled PuO_2. This information would allow a manufacturer to modify the feed powder to enable the pressed pellets to be sintered at a high temperature (~1600°C) to reach the target density, in this case 85% TD. PuO_2 should be sintered to a temperature above the expected operating temperature to produce a stable pellet that will not further densify during its mission lifetime.

One problem with the cold press and sinter technique is that green (unsintered) pellets cannot be pressed to the final density, so press dies have to be tailor made for each product to allow for shrinkage. Typically, pellets can be pressed from 65% TD up to 75% TD in the green state. Then, during sintering, the pellet will densify by shrinking from 4 to 9% to reach the desired 85% TD. As the previous section discusses, if pellets can be pressed isostatically, there would be uniform shrinkage to reach the final density. This may work well for GPHS pellets; however, even standard uniaxial pressing may be acceptable if the diameter and length tolerance is sufficient. As presented in Section D3-1, uniaxial pressing introduces density and stress gradients in pellets that can lead to cracking and laminations. Problems can be minimized and sometimes eliminated by engineering the feed powder to flow uniformly into the press dies, reducing the fines present, lowering pressing pressure, and creating powders that have low elastic quality (won't spring back more than 1% while exiting a die).

Another problem is the pressable nature of the feed powder. The powder needs to hold together (adequate green strength) in the green state and be able to withstand handling during transfer to the sintering furnace. The powder should be engineered to be pressed to green densities over 65% TD. The closer the green pellets are to the final density, the easier it will be to manage shrinkage and final dimensions.

Uniaxial pressing typically results in green density variation between the ends and middle portion of the pellets (see Figure D3-2). During sintering of MOX pellets, the pellets shrink to achieve a uniform density throughout. But because of the nonuniform green density, the diameter will become smaller in the middle. This is readily managed in the nuclear industry because sintered pellets are ground to a final uniform diameter. Approximately 0.002 in. are removed in a pellet that is 0.400 inches long. $^{238}PuO_2$ pellets will not be ground, so they must be sintered directly to the final desired size. The typical dimensions of a GPHS pellet are 1.085-in. diameter and length.

Analysis of the Los Alamos GPHS pellet specifications for dimensions and density led to the conclusion that green pressing and pressureless sintering could produce a pellet that meets all dimensional requirements without postsintering adjustments (grinding).

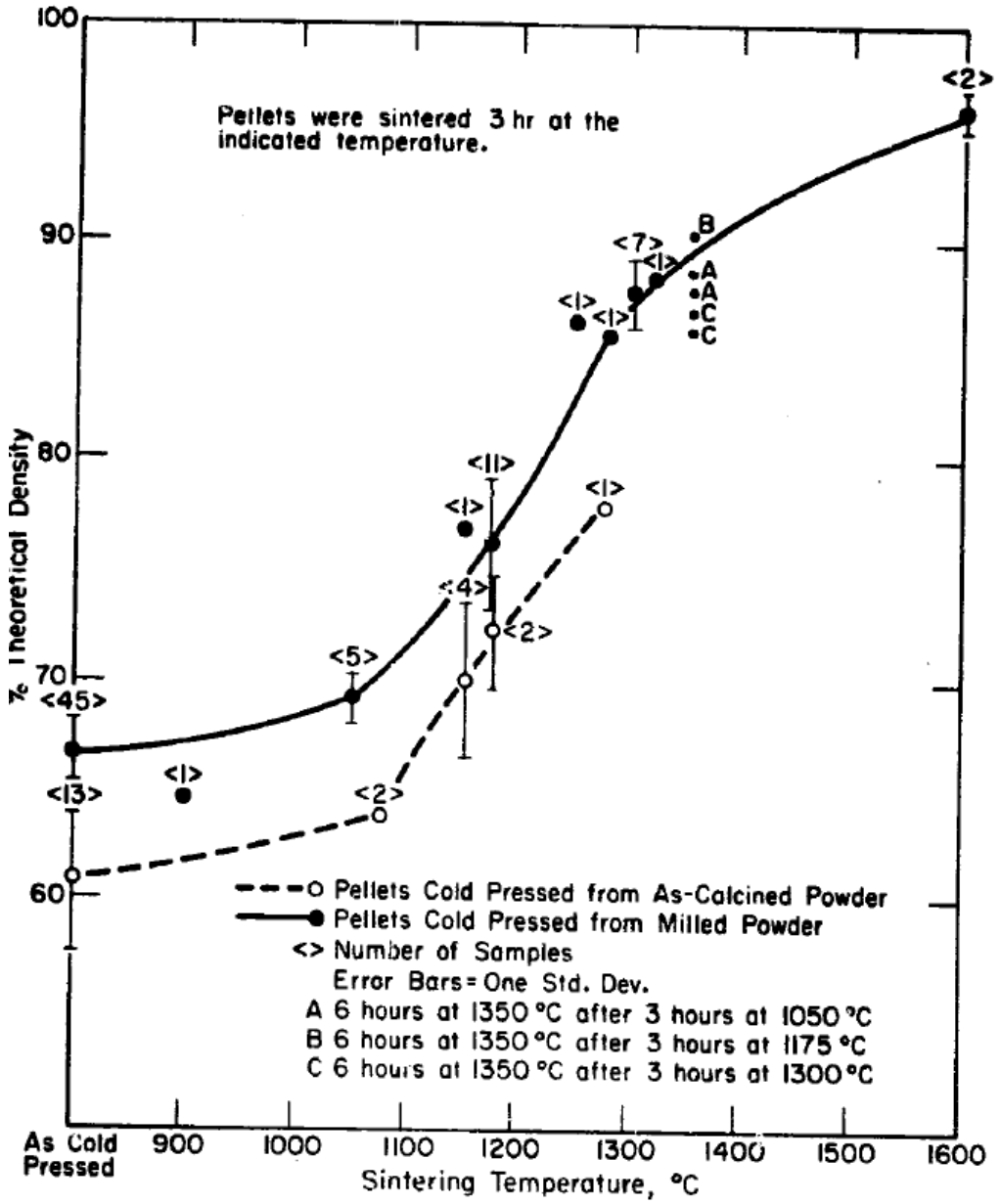

Figure D3-9. Effect of sintering temperature on densities of cold-pressed pellets.

The dimensions with tolerances of a typical GPHS pellet are presented in Figure D3-10. Length can vary up to 0.030 in These allowable ranges provide the manufacturer latitude to press and sinter an acceptable product. Figure D3-10 also shows the tapers expected after sintering, owing to green density variation across the pellet. The 0.002 to 0.0025 in. taper represents diameter variation of 0.004 to 0.005 in. This variation is well within the allowed diameter variation of 0.018 in.. Data used to perform this analysis came from the calculated values in Table D3-1. The table presents assumed green densities and the percent shrinkage, and dimensional change that would result from densification to a final density of 85% TD. A range of green densities are presented to calculate the different shrinkage expected, based on the green density variation in the pressed pellets and hence the expected diameter tapers. Because of the nature of biaxial pressing, there will be less variation in length from the middle to the exterior of the pellet. But this can be compensated for with end punch design.

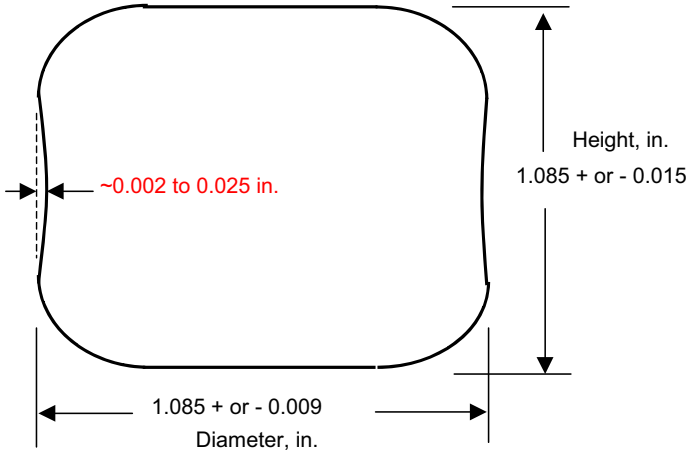

Figure D3-10. Dimensions of a sintered GPHS pellet with the expected taper resulting from pressing and pressureless sintering.

Table D3-1. Shrinkage and diameter change resulting from achieving the final density of 85% TD.

Green density	65% TD	67% TD	69% TD	70% TD	71% TD	73% TD	75% TD
Δ, inch	0.0400	0.0353	0.0307	0.0286	0.0264	0.0222	0.0182
% shinkage	8.55	7.62	6.71	6.27	5.82	4.95	4.09

For pressureless sintering, the pressing operation has to be coupled closely to achieve a specific size, density, and stable product. The pellet must be sintered at a high enough temperature so that the pellet is stable and will not continue to densify during operation. The pellet should be pressed at the highest green density possible to minimize shrinkage and maximize dimensional control. The powder should be formed to minimize elastic behavior during compacting. Some elastic spring back can be accommodated when using an exit taper in the die body. Typically, if a green pellet expands greater than 1% during exit from the die, laminations can occur.

D3-2.1 Cold Press and Sinter References

1. D. F. Bickford, D. T. Rankin, and P. K. Smith, “Preparation, Microstructures, and Properties of PuO_2,” *Sixth International Materials Symposium, University of California, Berkeley, California, August 24-27, 1976*.

Appendix D4
Superplastic Forming

D4-1. STUDY OF SUPERPLASTIC FORMING OF ZrO_2

A study by Auechalitanukul[1] is reviewed here briefly because it offers insight into the kinetics of superplastic forming. The study was performed on tetragonal polycrystalline zirconia (TZP), a well-known superplastic ceramic. In this study, spray dried granules (TOSO 3Y TZP) were sintered at 1400ºC for 2 hours. Figure D4-1(a) shows the appearance of the granules after sintering. The grain size of the granules after sintering was 0.3 μm. This fine grain diameter is a prerequisite for superplastic behavior and rapid densification. Several different size granules were hot pressed into cylinders at 1350ºC and 40 MPa. The microstructure of the granules during the intermediate stage of hot pressing (~85% dense) is shown in Figure D4-1(b) and illustrates how superplastic deformation allows ductile granules to deform into each other, resulting in densification and strong bonding between granules.

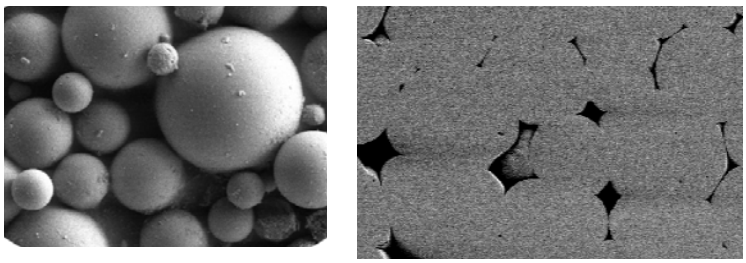

Figure D4-1. (a) Spray dried granules sintered at 1400ºC for 2 hours, and (b) during intermediate stages of hot pressing.[3]

Figure D4-2 shows the rate of densification is independent of the granule size.

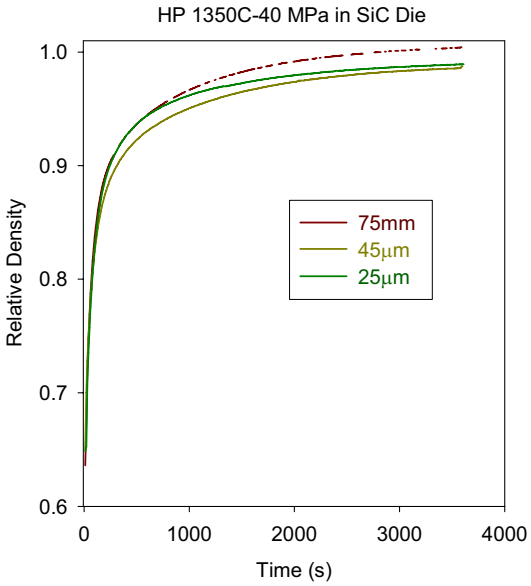

Figure D4-2. Density versus time curve for Y-TZP granules of several sizes.[3]

The densification rate is mainly dependent on temperature, pressure, density and grain size within the granules. The densification rate, $\dot{\rho}$, of these YTZP granules was shown to follow the Helle et al[2] equations.

$$\dot{\rho} = 3.1\rho^{\frac{2}{3}}\rho_0^{\frac{1}{3}}B\left(\frac{\sigma_a}{3\rho^2}\right)^n\left(\frac{1-\rho_0}{\rho-\rho_0}\right)^{n-\frac{1}{2}}$$

where

ρ_0 is the initial relative density, σ_a is the applied stress, and B can be determined from the superplastic creep rate equation,[3]

$$B = \frac{2x10^7 G\Omega D_{Zr}^{\ell}}{kTd^2}$$

where

G is the shear modulus, Ω is the vacancy volume, D_{Zr}^{ℓ} is the Zr ion lattice self diffusion coefficient, k is the Boltzmann constant, T is the temperature, and d is the grain size.[3]

Conclusions of this study can be related to hot pressing of GPHS pellet fabrication. Provided the grain size of the granules is sufficiently small, there is no need for 1100ºC sintered granules of $^{238}PuO_2$. The granules do not need to have any sintering activity because densification occurs by deformation of the granules rather than by sintering. Furthermore, there should be no postpress shrinkage. Pressure is required for shrinkage as long as the granules are well sintered. Another conclusion is that densification kinetics are not dependent on granule size. Thus, size of granules may be chosen only on the basis of optimum packing.

D4-1.1 Superplastic Forming References

1. Auechalitanukul, C., Ph.D. Thesis, *Hot Pressing Densification of Spherical Polycrystalline Particles of Superplastic Zirconia*, Rutgers University, 2006.
2. Helle, A. S., Easterling, K. E., Ashby, M. F., "Hot-Isostatic Pressing Diagrams: New Developments," *Acta Metallurgica*, Vol. 33, No. 12, 1985, pp. 2163-2174.
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Appendix E

Alternate Isotope Considerations

Appendix E
Alternate Isotope Considerations

E-1. ISOTOPE SELECTION

Numerous isotope studies have been conducted for heat source applications.[1,2,3,4] The selection of an isotope for outer planetary missions, beyond Mars, will be summarized here. Several competing factors must be considered in selecting an isotope for a heat source. They are:

1. Radiological half-life
2. Radiation fields generated by the material
3. Method of isotope production
4. Power density of the material
5. Reactivity and stability of the fuel.

E-1.1 Radiological Half-life

Radiological half-life is the time it takes for one half of an initial amount of a radioisotope to decay. (The material releases energy at one-half the rate it originally did.) Therefore, the half-life must be compatible with the intended mission life. Typically, the half-life should be at least equal to mission duration and preferably longer. If the half-life is too short, excess fuel is needed to assure sufficient power at the end of the mission and power leveling must be considered. The excess fuel produces excess heat, which must be expelled during the early phase of the mission. On the other end, if the half-life is too long, additional material is required to produce sufficient frequency of decay events and generate the required power. This approach makes the heat source larger or heavier than necessary. For outer planetary missions, NASA estimates mission durations to be 15 to 25 years. Therefore, an isotope should have a radiological half-life between 15 and 100 years.

Of the thousands of radioisotopes, only 20 fit within the 15–100 year range of half-life. Table E-1 lists them.

E-1.2 Radiation

The type and amount of radiation emitted by an isotope is essential to proper operation of an RTG. The four types of radiation are: alpha, beta, gamma and neutron. For RTG applications, alpha radiation is preferred because it is easy to shield. Beta radiation is also easily shielded; however, as the beta particle slows and releases its energy, it also produces Bremsstrahlung x-ray radiation. Gamma and x-ray radiation are undesirable to space applications because of the dose absorbed by personnel during production, assembly, and testing of the heat sources, interference with mission instrumentation on the spacecraft, and potential exposure to the general public if the launch fails. Neutron radiation requires hydrogenous material for shielding, and collecting heat is difficult in a small system.

Of the 20 isotopes with applicable half-lives, only six have alpha emission as their primary decay mode and receive valid consideration for outer planetary RTGs. They are Gd-148, Po-209, Cm-243, Cm-244, U-232, and Pu-238. Cm-243 is not acceptable because it also decays a quarter of the time by releasing a medium energy gamma that is three orders of magnitude higher than Cm-244 and Pu-238. While by itself U-232 has excellent performance characteristics as a heat source, its decay products include high-energy gamma emitters including Tl-208 and Bi-212. U-232 is the daughter product of Pu-236, which is why the current RTG material specification places a tight limit, 2 μg/g, on the quantity of Pu-236 permitted in Pu-238. Po-209 decays 0.48% of the time by releasing a 1.9 MeV beta particle. The beta decay produces appreciable x-ray radiation.

Of the six alpha-emitting isotopes, Gd-148, Po-209, Cm-244, and Pu-238 do not produce significant gamma emissions. Neutron emissions are another radiation concern. The neutron generation of Cm-244 is roughly 2,000 times that for Pu-238 when compared by disintegrations/g. Also, the gamma production of Cm-244 is approximately 160 times that for Pu-238.

Gd-148 and Po-209 alpha energy is only 3.5 MeV compared to 5.5 MeV for Pu-238. Therefore, 60% more material is required to produce the same amount of heat. These are light isotopes having less than the average number of neutrons. There is no simple means of producing this material. While the isotopes can theoretically be produced using heavy ions in a particle accelerator, there is no known method to produce the comparatively large quantities required for the RPS program. Therefore, Pu-238 is the preferred isotope as a heat source for outer planetary missions.

The radiation type and levels produced by the potential RTG isotopes are listed in Table E-1.

Table E-1. Isotope selection for outer planetary RTGs.

Isotope	Half-life (years)	Primary Decay Mode	Secondary Decay Mode	Neutron Dose Rate (mr/hr-gm@ 1m)
Promethium-145 (Pm-145)	17.7	Gamma		
Curium-244 (Cm-244)	18.11	Alpha	Spont. Fission	10.6
Strontium-90 (SR-90)	28.6	Beta		
Actinium-227 (Ac-227)	21.77	Beta	Alpha	
Lead-210 (Pb-210)	22.26	Beta	Alpha	
Curium-243 (Cm-243)	28.5	Alpha	Gamma	
Cesium-137 (Cs-137)	30.17	Beta	Gamma	
Argon-42 (Ar-42)	33	Beta		
Bismuth-207 (Bi-207)	33.4	Gamma		
Europium-150 (Eu-150)	36.9	Gamma		
Titanium-44 (Ti-44)	47.3	Gamma		
Platinum-193 (Pt-193)	50	Gamma		
Uranium-232 (U-232)	72	Alpha	Daughter products emit gamma rays	
Tin-121 (Sn-121)	76	Beta		
Terbium-157 (Tb-157)	71	Beta		
Gadolinium-148 (Gd-148)	74.6	Alpha		
Plutonium-238 (Pu-238)	87.75	Alpha	Spont. Fission	0.0057
Samarium-151 (Sm-151)	90	Beta		
Nickel-63 (Ni-63)	100.1	Beta		
Polonium-209 (Po-209)	102	Alpha	Beta	

E-2. REFERENCES

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Appendix F

Material Handling Improvements

Appendix F
Material Handling Improvements

F-1. MATERIAL HANDLING

F-1.1 Highly Enclosed Processing

Plutonium-bearing materials processing will be performed in gloveboxes that separate personnel from the radiation source, to maintain worker radiation exposure within guidelines established by the Department of Energy.[1] Containment valves, remote-handling devices, sealed processing, and containments (i.e., glovebags and gloveboxes) will be used to minimize worker exposure. Enclosed processing within the glovebox could be used to minimize worker exposure, loss of product, and reduce cost of cleanup and decontamination activities.

F-1.1.1 High Containment Valve

High-containment split butterfly valves (see Figure F-1) provide minimal risk to product contamination or worker exposure because of the direct metal-to metal seal. The sealed environment within the containment valve, fitted with a pressure/vacuum plug, is comparable to that of a high-specification compression fitting with a maximum helium leak rate of 4.0×10^{-9} cc/sec. The containment valves have been used successfully in the pharmaceutical industry, transferring toxic powders down to nanogram levels. The high-containment valve is easily cleaned. Containers fitted with the valves could be used to transfer product from one process operation to the next with minimal release to the glovebox atmosphere. Movement of the containers could be manual or automated.

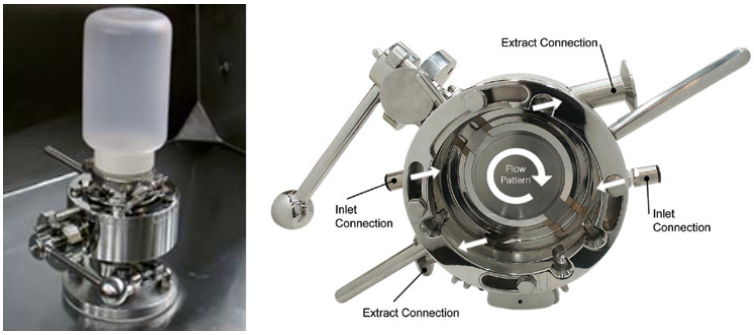


Figure F-1. Containment split butterfly valve.

F-1.1.2 Rapid Transfer Ports

Rapid transfer ports are used for the transfer of toxic products and are made up of two parts (see Figure F-2). The fixed part is mounted on the wall of the isolator, and the mobile part is sealed to the rigid or flexible container. The concept is that two sealings meet at a point with four elements mutually shielding each other's faces, locked together by rotation of the mobile port.

Figure F-2. Rapid transfer ports.

F-1.1.3 Liner

Liners consisting of stainless steel chutes with surrounding liner cartridges are another method to transfer toxic powders. The liner is fixed to the chute via a top and bottom ring, both outside the powder flow.

F-1.1.4 Hypalon® Gloves and Seals

The majority of glovebox breaches occur from glove damage. Various materials were studied in a radiological environment to determine the safest glove materials for handling plutonium. Results from neutron degradation studies indicate that Hypalon/polyurethane gloves should be considered for radiological glovebox operations, but pure Hypalon gloves should be the glove of choice for applications involving high neutron fluxes.[5] Hypalon could be evaluated for other glovebox sealing applications.

F-1.2 Gravity Flow

Bins, chutes, and hoppers are used for the benefit of highly enclosed processing. A particular process operation may be arranged below a preceding operation, and process flow is simply achieved by gravity. Minimizing and mitigating plugging, bridging, arching, and rat holing will likely be technically challenging. Minimizing product holdup will also be an issue. Bins, chutes and hoppers may be constructed of glass for viewing pluggage and to aid cleanout operations. Carefully designed glass components should not be more vulnerable to breakage than the glovebox windows.

F-1.3 Pneumatic Conveying

An important material-handling technique is moving material suspended in a stream of air over horizontal and vertical distances from a few to several hundred feet by a pneumatic conveying system.[2] This system could be closed to minimize release and loss of product. Glass pipe and tubing may be included for visual indication of hold-up and impending plugs.

F-1.4 Screw Conveyors, Mixers, and Feeders

The screw conveyor is a common and possibly the most versatile conveyor type. Screw conveyors consist of a helicoid flight turning in a tube or trough. In this application, the tube or trough would be sealed from the glovebox interior atmosphere. Power to convey is transmitted through the helicoid flight member and is thus limited by the allowable size of the member.

Because of their versatility, screw conveyors can be adapted to a wide variety of processing operations. Using screw conveyors as mixers and feeders could likely benefit this application.

F-1.5 Vacuum Dust Collection

A vacuum dust collection system may be used with dust pickup nozzles strategically located at points in the process susceptible to dust emissions, such as at dynamic seals or openings.

F-1.6 Magnetic-Coupled Drives and Components

Magnetic-coupled drives and components may be used for the benefit of highly enclosed and sealed processing (see Figure F-3). Magnetic-coupled drives transmit force across a sealed containment barrier without a direct mechanical connection. They are usually made from two concentric rings, but other arrangements (such as identical flat rings facing each other) are not uncommon. Either rotary or linear motion can be transmitted. Magnetic-coupled drives have been successfully used in pumps, blowers, autoclaves, mixers, etc.

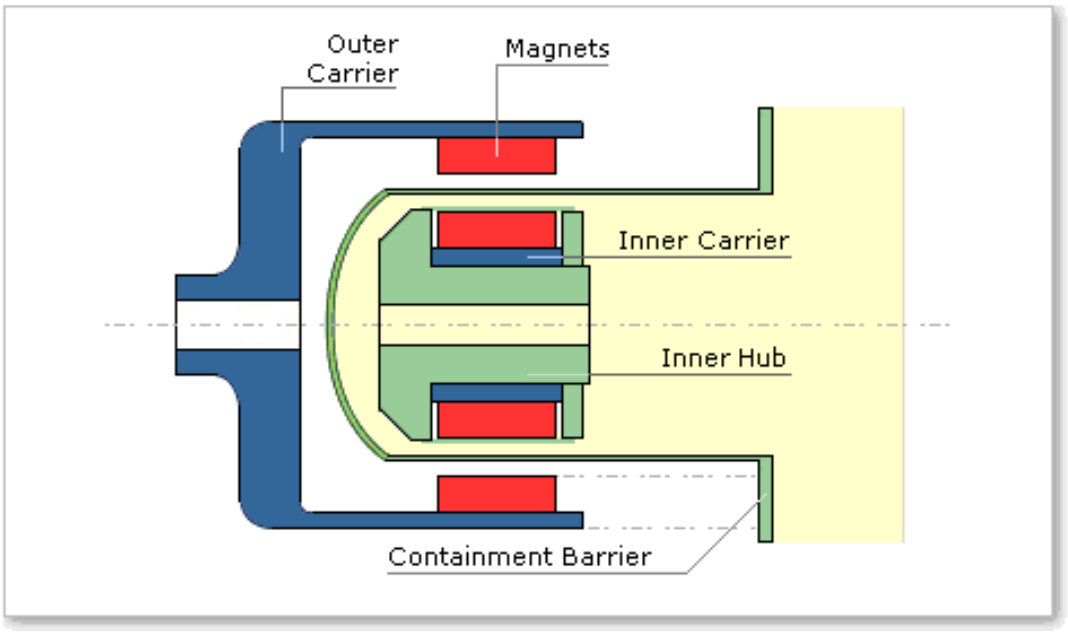


Figure F-3. Rotary magnetic-coupled drive.

F-1.7 Cleanout Devices and Techniques

Various process cleanout devices such as rods, pokers, and scrapers may be used in this system if fouling inhibits material flow, or for other maintenance activities as necessary. Built-in ports could allow access to areas where maintenance activities are likely needed and would otherwise be difficult to reach.

Cryogenic flushing using liquid argon or liquid nitrogen may be an option for cleaning out a mill by effectively washing material particles from inside the equipment. The cryogen flushing agent could be introduced into the mill after the particle size reduction step is complete, to capture the residual particles adhered within the mill. Before the slugging and screening phase of the process, the slurry would be returned to ambient temperature with the cryogenic flushing agent vaporizing and leaving the particulates to be slugged. Airborne particles would be filtered for reintroduction to the process.

F-2. PARTICLE SIZE REDUCTION

F-2.1 Ball Milling

Ball mills are cylindrical devices used for pulverizing soft, fibrous, hard, and brittle materials. Ball mills rotate around a horizontal or vertical axis, partially filled with the material to be ground plus the grinding medium. According to experts, the most efficient fill level for a ball mill is to load material equal to 25% of the total volume of the mill. A 40% batch will take twice as long to mill as does the 25% batch. But depending on the cycle time and unit operations, it may actually be more economical to operate with the "wrong" batch size. Industrial ball mills can operate continuously, fed at one end and discharged at the other end. Large to medium-sized ball mills are mechanically rotated on their axes, but small ones normally consist of a cylindrical-capped container that sits on two drive shafts (pulleys and belts are used to transmit rotary motion).

F-2.1.1 Planetary Ball Mills

Planetary ball mills have the capability to grind material to less than 1 µm and, for colloidal material, to less than 0.1 µm (see Figure F-4). The feed material may be soft, hard, brittle, fibrous and either dry or wet.

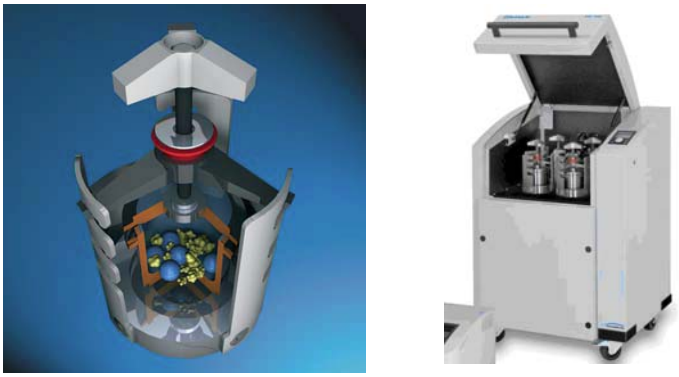


Figure F-4. Planetary ball mill.

Grinding jars are arranged eccentrically on the sun wheel of the planetary ball mill. The direction of movement of the sun wheel is opposite to that of the grinding jars in the ratio 1:-2 (or 1:-2.5 or 1:-3). The grinding balls in the jars are subjected to superimposed rotational movements, the so-called Coriolis forces. The difference in speeds between the balls and grinding jars produces an interaction between frictional and impact forces, which releases high dynamic energies. The interplay between these forces produces the high and very effective degree of size reduction of the planetary ball mill. The centrifugal forces produced by the rotation force the sample and the grinding balls against the inner wall of the grinding jar, where size reduction takes place primarily by pressure and friction.

The working principle of the planetary ball mills is based on the relative rotational movement between the grinding jar and the sun wheel. In addition to the sun wheel diameter and speed of rotation, this speed ratio is decisive for the energy input and therefore for the results of the size-reduction process. The higher the speed ratio, the more energy is generated. There are planetary ball mills with different speed ratio settings. For example, a ratio of 1:-1 means that each time that the sun wheel rotates, the grinding jar also rotates exactly once in the opposite direction. With a speed ratio of 1:-2 the grinding jar rotates twice for each sun wheel rotation. To follow the rotational movement of the grinding jar, imagine you are standing at the center of the sun wheel.

The grinding jars range from 12 ml to 500 ml in volume, with material composition from hardened steel, stainless steel, tungsten carbide, agate, sintered aluminum oxide and zirconium oxide. The ball diameters range from 10 mm to 40 mm. Planetary ball mills have a graphics display with one button operation for speed, grinding time, energy input, grinding direction reversal with selection of running and pause times, start time, remaining running time, etc. Ten combinations of speed, grinding time, and interval settings can be stored for repetitive grinding tasks.

F-2.1.2 Mixer Mills

The grinding jars perform oscillations in a horizontal position. The inertia of the grinding balls causes them to impact with high energy on the sample material at the rounded ends of the grinding jars and pulverize it (see Figure F-5). Also, the movement of the grinding jars combined with the movement of the balls result in the intensive mixing of the sample. The degree of mixing can be increased even further by using several smaller balls. If many very small balls are used (e.g., glass beads), biological cells can be disrupted. The large frictional impact between the beads ensure effective cell disruption. The final material fineness is approximately 10 µm.

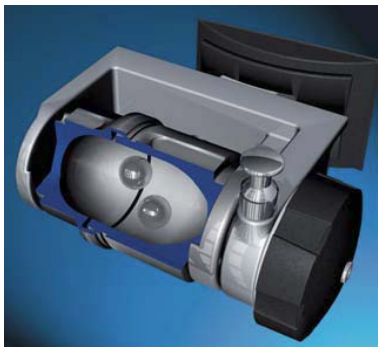


Figure F-5. Mixer ball mills.

F-2.1.3 Cryogenic/Mixer Mills

Cryogenics may be used before grinding with ball mills to decrease time required to reduce the size of the powder.

Sample material and grinding ball charge are placed in the screw-top stainless steel grinding jars, which are then immersed in liquid nitrogen.

After cooling, they are fastened in the quick-clamping device, which holds the grinding jars securely even at extremely low temperatures. After a grinding time of only 2-3 minutes, a completely homogenized sample is obtained. This procedure saves time and is particularly economical because of the very low consumption of liquid nitrogen at the approximate temperature of -196°C.

Figure F-6. Liquid nitrogen bath.

Thermally sensitive and elastic substances can be successfully processed by external cooling of the grinding jars before grinding. However, jars made from agate or ceramics should not be cooled with liquid nitrogen to prevent their damage during the grinding process. The screw-top grinding jars are particularly suitable for cryogenic grinding because they remain hermetically sealed until they have regained room temperature. This prevents atmospheric humidity from condensing on the cold sample as water vapor, which could penetrate the sample and falsify the analytical results.

A cryogen may also be added directly to the material within the grinding jar to create a wet milling process, which may decrease milling time and potentially reduce the final particle size.

F-2.2 Attrition Milling

Attrition dry grind processing is achieved by an expanded moving bed of media. The dry particles are subjected to impact, rotational, tumbling, and shear forces, making it possible to achieve micron range fine powders. The attrition dry grinding is versatile because of the ability to modify many variables such as grinding media size, type, and amount, machine speeds, and feed rates. This process is achieved in a stationary tank with a rotating shaft and arms that agitate the media into a random state of motion called kinematic porosity. The media and particles are free to move, collide, and impinge upon each other, generating high shear and powerful impact for efficient grinding. This process can be operated in continuous or batch grinding processes. Continuous dry grinding is chosen for the following reasons:

- Large production quantity is required.
- Material is temperature sensitive.
- Material has a tendency to cake.

Batch dry grinding is chosen when the material requires a longer residency time (more than 30 minutes), and the prime consideration is the finest particle size possible with the ability to control the milling atmosphere. The grinding tank cover may be equipped with a mechanical shaft seal. An inert gas purge allows the material to grind under an oxygen-free condition.[4] Mills may be placed in series to ensure a finer material size. Particle sizes as low as 1.1 µm have been attained with this method.

F-2.2.1 Fluidized Bed Jet Mill

Relying purely on particle-to-particle attrition in the center of a fluidized bed of material, this is achieved by focusing three or more compressed gas nozzles into the milling chamber, which accelerates the particles to produce collisions where energy is released, causing particle breakdown (see Figures F-7 and F-8).

Powder finenesses of ranges from 2 to 200 µm have been attained.

Figure F-7. Fluidized bed jet mill.

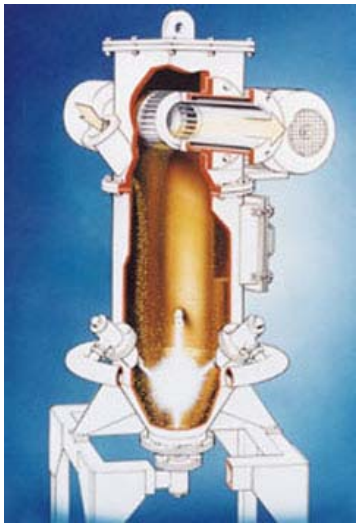


Figure F-8. Schematic of fluidized bed jet mill.

F-2.2.2 Dry Agitated Pearl Mill

The dry agitated pearl mill consists of a water-cooled vertical cylinder, typically lined with aluminum tiles and top driven wear-protected motor. Incoming material at minus 200 µm or finer, and grinding media are introduced at a controlled rate from above and move through the machine by gravity. Size reduction occurs because of the shear force caused by agitation of the grinding media and material.

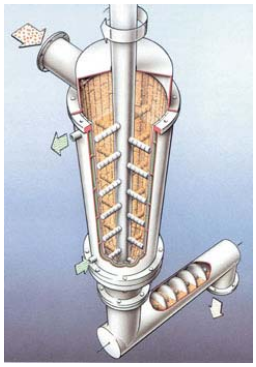


Figure F-9. Dry agitated pearl mill.

F-2.3 Granulation

F-2.3.1 Dry Granulation/Roll Compaction

Fine powders can be processed into densified sheets by using mechanical pressure exerted on two compacting rolls (see Figure F-10). The densified sheets can then be granulated to any desired mesh size. The particle size range of the product can be selected to suit individual requirements and varied according to process needs. Cross contamination and product loss can be reduced. Higher flow rates and more even fill can be achieved. The basic concept of compaction (seen in the figure) is to force fine powders between two counter-rotating rolls. As the volume decreases through the region of maximum pressure, the material is formed into a solid compact or sheet. Some of the factors controlling the compaction process are roll surface, diameter, peripheral speed, separating force or pressure capabilities, feed screw design and basic compaction characteristics of material being processed. The product may be compacted by the granulator to a uniform particle size distribution. This can be achieved with a granulator that is designed with maximum flexibility, enabling control of the size reduction of the compacted product with predictable and repeatable results. To minimize fines and overs, it is possible to design the dry granulation system to include a screener and recycle system. This provides tremendous control of the final particle size and density.

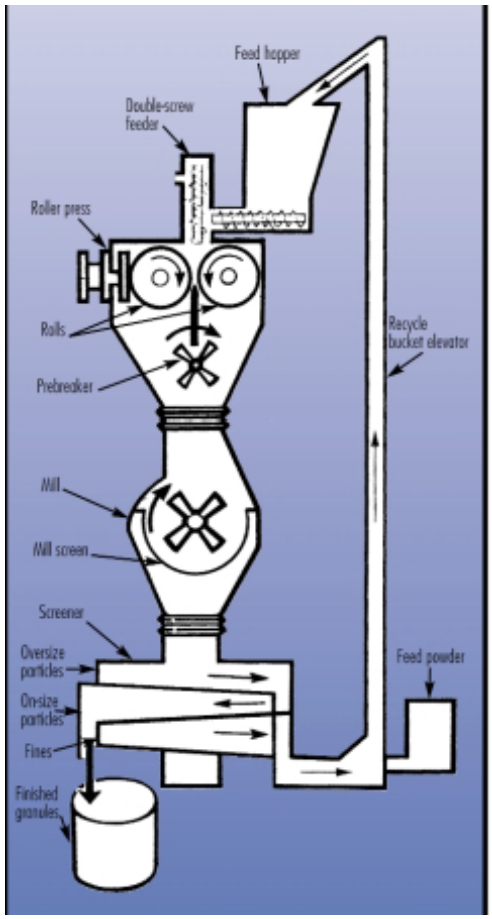


Figure F-10. Compaction-granulation system.

F-2.3.2 Wet Granulation

A spray granulator allows a liquid solution to be rapidly dried over an active ingredient. This newly encapsulated particle structure is harder and denser, yielding particle properties that are desirable in many applications. The newly formed particle can be sprayed again and again, creating larger and larger spherical pellets that form in successive onion-like layers (see Figure F-11).

Figure F-11. Spray granulation process.

Most spray granulators spray a liquid solution over a hot fluidized bed of active material. This process works by suspending and tumbling the particles in a high-velocity gas flow while applying the coating as a fine mist. Both liquid and solid powder coatings may be applied in this type of process.

Some of the desirable product properties of granulator processing are:

- Narrow grain size distribution
- Dust-free granules
- Spherical pellets
- Free-flowing properties
- Good dosing properties for pharmaceuticals
- Good dispersion
- Good solubility
- Compact structure
- Less hygroscopic
- Low bulk density
- Less abrasive.

In a spray granulator, the particles are conveyed through the inner partition into the expansion chamber by the hot, fluidizing air. Gravity overcomes the force of the fluidized air and the particles fall back into the outer partition. The pneumatic atomizing nozzle in the bottom center of the chamber introduces the coating solution. This nozzle sprays upward providing successive applications of coating (see Figure F-12).

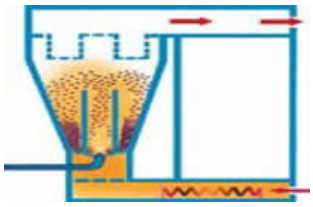


Figure F-12. Spray granulator.

F-3. POWDER CHARACTERIZATION

F-3.1 Digital Image Processing

Focused ion beam (FIB) is a very effective workbench for microstructured devices. These can be built, modified, cross-sectioned or micropolished in dimensions between about 10 nm and 100 µm. Both milling (etching) of nearly any material and depositions (tungsten, platinum, or Si-dioxide) are possible as well as direct imaging in a quality comparable to high-resolution scanning electron microscopes.

Milling processes can be enhanced or slowed down by suitable gas chemistry, allowing material-selective microetching. In summary, FIBs open up new prospects in material science, like target preparation of cross sections resulting in high phase contrast two- or three-dimensional images, which are indispensable in the micro- and nanotechnologies. In this context, FIB technology also enables sample preparation with phases of extremely different hardness without smearing or producing artifacts, though it has to be noted that the ion beam amorphizes and contaminates some atomic layers at the surface. The combination of an electron and an ion column within an advanced dual beam FIB system allows better control of possible defects. Sophisticated applications are in materials and life science as well as in micro/nano electronics and photonics.[3]

Digital image processing is the use of computer algorithms to perform image processing on digital images. As a subfield, digital image processing has many advantages over analog image processing; it allows a much wider range of algorithms to be applied to the input data, and can avoid problems such as the build-up of noise and signal distortion during processing.

Image analysis can be used to measure particle size from 0.7 µm to 2 mm. By its very nature its dynamic range is more limited than with the other, ensemble techniques. But the range can be extended by combining data obtained at several magnification intervals.

Image analysis systems capture a two-dimensional image of the 3D particle and calculate various particle size and particle shape parameters from this 2-D image. Calculating size and shape parameters like the ones shown in the list below allow even the most subtle differences to be identified and quantified.

F-3.1.1 Digital Imaging Processor

The digital imaging processor analyzes both the particle size and shape ranging from 0.5 µm to 3000 µm, depending on material properties and dispersion conditions (see Figure F-13).

Figure F-13. Digital imaging processor.

- Fully integrated dry powder disperser. A novel, fully integrated dry powder dispersion system reduces sample preparation times and significantly improves the repeatability of measurements.
- Statistical significance. Analyzes hundreds of thousands of particles with a single click of the mouse.
- No more user bias: the standard operating procedures approach allows all instrument variables (focus, light intensity, magnification, etc.) to be objectively recorded and controlled. Methods developed on one instrument can be transferred electronically around the globe in a single file.

- Save high-quality images. The ability to see and record an image of every individual particle enables a visual verification of phenomena such as the presence of broken particles, agglomerates, fines, foreign particles, etc.
  - Accurate, repeatable,[1] and 'validatable.' To ensure data integrity, the image analysis system automatically calibrates before and after every particle analysis using a multi-pitch grating traceable to the National Physical Laboratory. The image analyzer conforms to 21 *Code of Federal Regulations* Part 11 requirements, and full installation qualification/operational qualification documentation is available.

F-3.1.2 Digital Imaging Processor Analysis Software

The excellence of the digital imaging processor can only be fully realized with advanced, dedicated image analysis software. The full value of such a system is fully captured when the software is high-quality, refined, automated, easy to use, fit-for-purpose and dedicated to particle characterization analysis rather than general purpose.

As standard, the digital imaging processor software enables:

- Intuitive and user-friendly operation
- Standard operating procedures, for repeatability between operators, image analysis systems, and sites
- Scattergram, for easy visualization of measurement data, classification, and filtering (see Figure F-14)
- Data comparison, to compare and cluster data to find differences or similarities between multiple measurements
- Manual mode, which uses the image analysis system as a manual microscope for method development purposes
- Custom reports, to suit every laboratory's requirements
- Particle viewer, to view, sort, filter, and classify all captured particle images
- Selected parameter trend analysis, to plot trends between multiple records
- Result overplots and statistical plotting, to overplot and compare multiple results.[3]

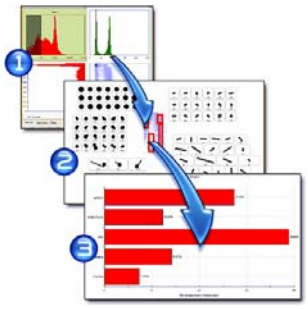


Figure F-14. Scattergram.

F-3.1.3 Automated Microscope Sample Dispersion Unit

Reliable measurement of dry powders requires strict control of dispersion conditions. A novel, fully integrated, software-controlled dry powder dispersion system (see Figure F-15) reduces sample preparation times and significantly improves the reproducibility of measurements.

The sample is dispersed with an instantaneous pulse of compressed air. Precise control of dispersion pressure, injection time, and settling time ensures highly reproducible measurements across a broad range of samples.

Figure F-15. Sample dispersion unit.

Measurements are made in an enclosed sample carrier, minimizing environmental exposure and ensuring safe material handling, especially when measuring toxic materials samples. Multiple aliquots can be prepared in advance, ready to use at the next measurement.

F-3.2 Laser Spectrometry

The technique of laser diffraction relies on the fact that particles passing through a laser beam scatter light at an angle that is inversely proportional to their size (small particles scatter light at high angles whereas large particles scatter light at low angles). It is therefore possible to calculate particle size distribution if the intensity of light scattered from a sample is measured as a function of angle. This angular information needs to be compared with a scattering model (Mie theory), to calculate the size distribution. The technique has a very large dynamic range, from 3.5 mm to below 100 nm, as defined by the range of angles over which the scattering pattern is collected and the instruments' optical configuration. (See Figure F-16.)

The laser diffraction technique is flexible in terms of the type of samples that can be measured. Particles can be dispersed in a liquid medium (wet laser diffraction) or as solid particles dispersed in an air stream (dry laser diffraction). Measurements are also possible on aerosol-based systems such as liquid atomizers and pharmaceutical inhalers. For wet analysis, samples require dilution to be measured. The sample concentration over which samples can be measured is approximately 50-1000 ppm.

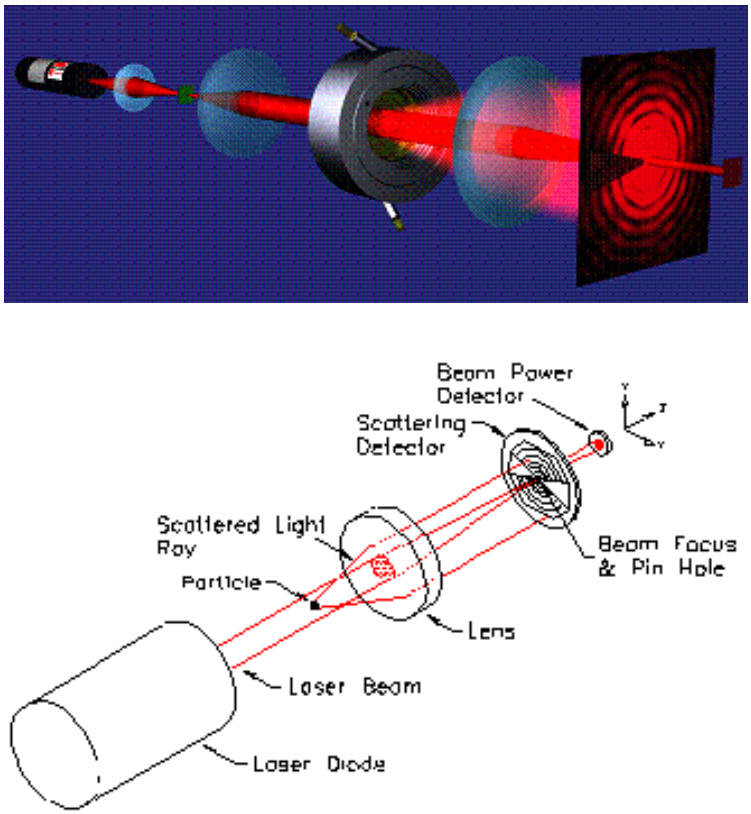


Figure F-16. Laser diffraction/Mie theory.

Laser diffraction is a proven and robust particle-measurement technique. It has many benefits in withstanding the demands of the process environment.

- Rigorous Mie light scattering theory allows determination of the complete particle size distribution
- No calibration required
- No long data acquisition intervals that can mask process behavior
- High concentration measurement.

A significant challenge for online analysis using laser diffraction is to accommodate the multiple scattering that takes place at the high particle concentrations encountered in a process line.

Where particle concentrations are low enough, turbidity is linear with concentration. However, this is not the situation at higher concentrations. Particles are so close together that the scattered radiation is rescattered by other particles.

This is not an issue in laboratory instruments because the user has control over the amount of sample measured. However, in a process instrument using continuous sampling techniques, measurement must be accurate even when higher loadings are present in the process stream. This is especially significant during plant start-up, shutdown and process changes.

Light from a laser is shone into a cloud of particles (e.g., cement), which are suspended in a transparent gas, (e.g., air). The particles scatter the light, smaller particles scattering the light at larger angles than bigger particles. The scattered light can be measured by a series of photodetectors placed at different angles. This is known as the diffraction pattern for the sample. The diffraction pattern can be used to measure the size of the particles using light scattering theory that was developed in the early 20th century by Mie. Because the instrument measures clouds of particles rather than individual ones, it is known as an "ensemble" technique, with the advantage that at smaller sizes (e.g., 10 μm), the system is measuring millions of particles, which gives statistical significance to the measured results.

Although several correlations and theories exist on light scattering, the most comprehensive and rigorous theory is that of Mie's, based on Maxwell's electromagnetic field equations. Two assumptions made in this theory are pertinent to the result obtained:

- **The particle is assumed to be spherical**

  This is important, because few particles are actually spherical. Laser diffraction is sensitive to the volume of the particle. For this reason, particle diameters are calculated from the measured volume of the particle, but assume a sphere of equivalent volume.

- **The suspension is dilute**

  The particle concentration is assumed to be so low that scattered radiation is directly measured by the detector (i.e., single scattering) and not rescattered by other particles before reaching the detector (i.e., multiple scattering).

- **Multiple scattering/high concentration particle sizing**

  If the particle concentration is low enough, then the instrument will follow Beer-Lambert's law, that is, the turbidity (i.e., log of the inverse of the transmission, or a measure of the incident light lost because of scattering) is linear with the concentration. However, there will come a point when Beer's law no longer holds, when the particles are so close to one another that scattered radiation is rescattered by other particles. Insitec uses a patented technique that can correct for the onset of multiple scattering, which effectively increases the concentration dynamic range of the instrument.

F-3.2.1 Particle Size Analyzer

The online particle size analyzer for hazardous environments (see Figure F-17) provides robust, reliable, online particle sizing for dry powder applications and is ideal for process optimization and control applications.

Compliance with the new ATEX regulations (99/92/EC and 94/9/EC)–mandatory for existing workplaces from July 2006–results for the first time in the zoning of areas that are potentially explosive because of the presence of dust. The Insitec D has been approved for Zone 22 use (Category 3 approval).

Designed to International Electrotechnical Commission 61241, the safety of the instrument is ensured through protection by enclosure and by limiting maximum surface temperatures. With a maximum rated surface temperature of 120°C, the Insitec D is suitable for all dusts with a 5-mm layer temperature in excess of 195°C, making it suitable for challenging materials such as lignite.

Figure F-17. Online particle analyzer.

- ATEX approved Category 3 instruments for use in Zone 22 areas
- For flammable dusts
- Real-time particle size analyzer based on laser diffraction for particles in the size range 0.1 to 1000 µm
- Automatic continuous online operation, or manual at-line
- Full automation and integration into plant control systems
- RTSizer software interfaces with plant control systems through Malvern Link automation package
- Award-winning Intellution iFix SCADA license delivered with every process system. This gives enormous flexibility in controlling instrument, sampling system, and linking to the plant control system.

F-3.2.2 Process Optimization using Data Mining

The process optimization system provides continuous monitoring of particle size sample material by channeling the powder continuously through a bypass system running parallel to the main product stream. This method is more reliable and much quicker than laboratory measurements.

The sampling technique ensures real-time measurements under iso-kinetic conditions and thereby a full and accurate characterization of the particulate. Data from the particle size analyzer can be used manually or incorporated into the mill control system for automatic process control.

Using data mining systems, we are able to identify opportunities to improve performance from the analysis of operating data. Hosokawa Micron offers a suite of knowledge-based solutions and performance optimizers to provide intelligent monitoring, operator advice, fault diagnosis, and decision support.

Integrated software solutions are configured for each individual application with the aim of delivering immediate benefits with little or no capital expenditure.

A typical software package or “toolkit” can include:

- Data Mining-Software tools to allow ongoing analysis of operating data, typically using existing sensors and controls.
- Intelligent Monitoring-Online knowledge-based systems comparing plant performance with targets and highlighting poor performance.
- Advisory Systems- Online knowledge-based systems providing consistent and ongoing advice for operators and management.
- Fault Diagnosis-Online advice for operators and management about plant faults and potential areas of failure or mal-operation.
- Optimization-Providing advice on more effective ways to operate process and plant.

F-3.2.3 Dry Sampling

Dry sampling a powder may be accomplished with a sensor in the process line. The sensor works on a fiber-optic patented measurement principle and simultaneously measures the size and velocity of individual particles (see Figure F-18). Statistical techniques associated with the technique allow calculation of chord length distributions. No calibration is required and constant measurement is allowed with no time gaps in the data. The sensor does not assume the particles are spherical. Size and velocity can be extracted from particles as they pass through a laser beam and cast shadows on to a linear array of optical fibers. A signal is generated owing to the particle crossing fiber bundles labeled “burst a” and “burst b.” The frequency of this signal is measured by photodetectors and is proportional to the particle velocity versus knowing the spatial filter constant g, the velocity v can be calculated. As the particle passes through the beam, a secondary pulse signal is generated by a single optical fiber. Knowing the time t of the pulse signal, and the velocity v of the moving particle, the chord length x of the particle can be calculated.

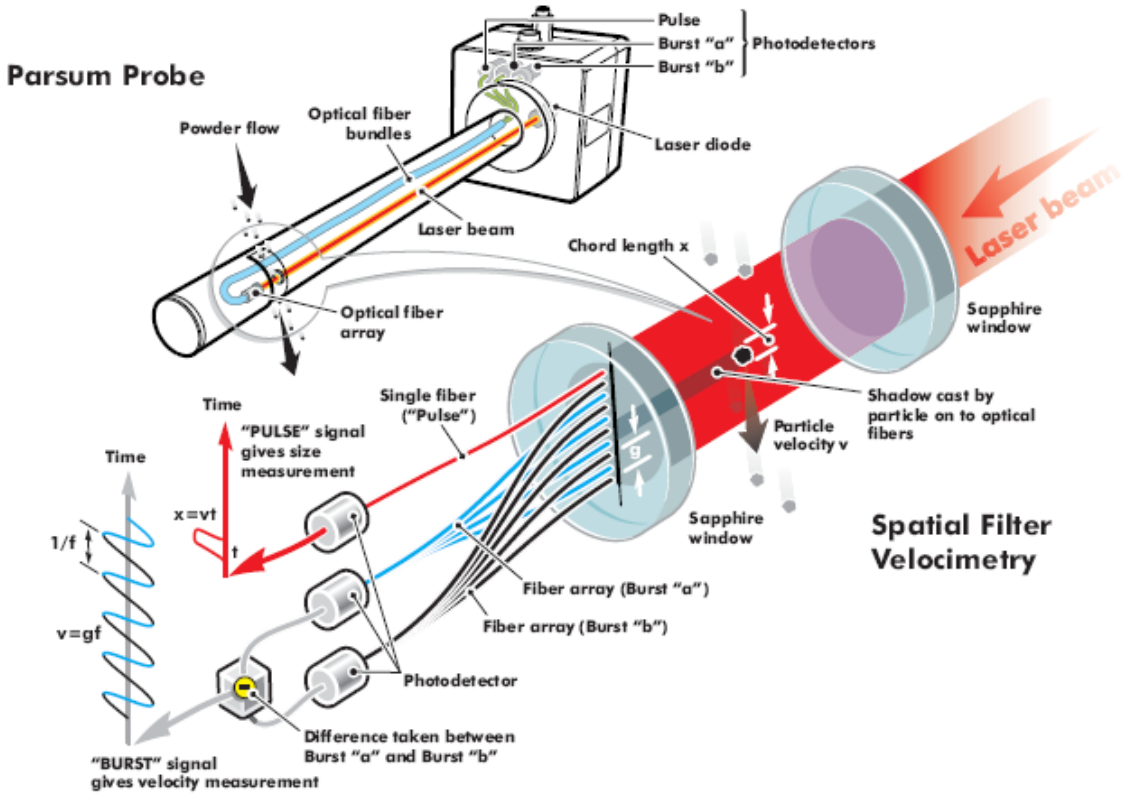


Figure F-18. Diagram showing the principle of operation of Spatial Filter Velocimetry in the Parsum probe.

F-3.3 Porosity/Differential Pressure

An online measurement of porosity is possible using a device that measures either air permeability or air resistance. A measurement sensor ensures measurement reliability and accuracy required for closed loop control of refining, filler, stock flow ratios, etc. (See Figure F-19.)

The porosity system monitors the time required for a known volume of air, under a known differential pressure, to pass through a given area of the moving web. The elapsed time is converted into porosity units.

Optionally, the device measures the volume of air passed through the web using the unique platform supporting full web slice integration of scanning systems.

The measurement sensor incorporates intelligent signal processing, and its automatic calibration maintenance and self-cleaning cycle will operate reliably in the manufacturing environment.

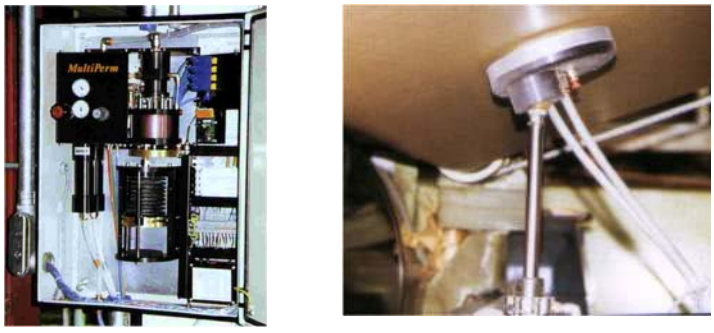


Figure F-19. Online porosity measurement.

The software platform provides data acquisition, analysis, presentation, and reporting for real-time online usage for the operating staff and long-term storage and grade data retrieval for management reporting and historical quality analysis.

F-4. REFERENCES

1. Brault, J. R., *Remote Material Handling in the Plutonium Immobilization Project*, Rev. 1, WSRC-TR-2000-00051, 2000, pp. 1-6, http://www.osti.gov/bridge.
2. Perry, R. H. and Don Green, *Perry's Chemical Engineer's Handbook*, 6th Edition, New York City, McGraw-Hill, Inc., 1984, pp. 7-1 through 7-20.
3. The Materials Science and Technology Institution of the ETH Domain Materials Design in the Nanometer Range.
4. Just, A. and Margaret Yang, "Attrition Dry Milling in Continuous and Batch Modes," *Ceramic Industry*, l997, http://www.unionprocess.com/tech.html.
5. Griffin, Matthew, *Evaluation of Hypalon® and Polyurethane for Use in Plutonium Glovebox Environments*, M.S. Thesis, University of Texas, Austin, May 2006, pp. 1-80.

Appendix G

Alternatives Evaluation Report

Appendix G
Alternatives Evaluation Report

This record tells the order for topics.

G-1. OBJECTIVES

The objectives for the workshop were:

- Identify preferred process technology for producing a granular/solid form of Pu-238 directly from a solution (eliminating the powder state).
- Identify preferred process technology for converting Pu-238 granules to pellets.

G-2. ATTENDEES

Name	Phone	E-Mail	Representing
Bickford, Dennis	803-257-6312	dennisbickford@bellsouth.net	Solidification (SRS)
Borland, Mark	208-533-7660	mark.borland@inl.gov	Team Lead, INL
Burke, Larry	208-526-6758	lawrence.burke@inl.gov	Health Physics, INL
Cannon, Roger	908-705-6031	wrcannon@fairpoint.net	Pellet Fab, Rutgers Univ.
Chidester, Ken	435-673-0684	kennfta@msn.com	Pellet Fabrication (LANL)
Cowell, Brian	865-574-0656	cowellbs@ornl.gov	ORNL
Frank, Steve	208-533-7391	steven.frank@inl.gov	Solidification Lead, INL
Friesen, Carl	208-526-1765	friesecd@id.doe.gov	DOE-ID
Johnson, Stephen	208-533-7496	stephen.johnson@inl.gov	INL
Lessing, Paul	208-526-8776	paul.lessing@inl.gov	Pellet Fabrication Lead, INL
Patton, Brad	865-574-6800	pattonbd@ornl.gov	ORNL
Wheeler, Tom	208-524-2286	thomas.wheeler2@inl.gov	Mechanical Eng., Walsh Eng.
Seward, Linda	208-680-2532	lcseward@msn.com	Facilitation
West, William	208-681-4672	bwest@polestar.com	Facilitation

G-3. ACTION ITEMS

The following actions were recorded during the course of the four-day workshop.

- Obtain micrographs from Mound records. Steve Frank-complete.
- Get a recent copy of the specification for this meeting. Mark Borland-complete.
- What types of measurement tools does LANL use for material characteristics? Mark Borland-complete.
- Contact ALCHEM on the fines question for carbonate alternative. Steve Frank.
- Develop a focused list of questions on the Russian process for S. Johnson to use during the Russian meeting in May. Mark Borland.

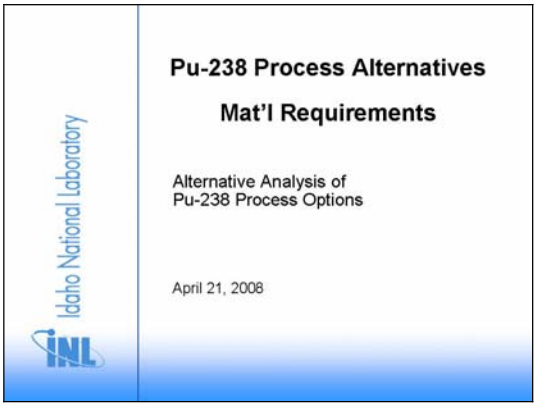
- Resin loading and conversion. Obtain information on carbon impurities and data on characterization. Brian Cowell.

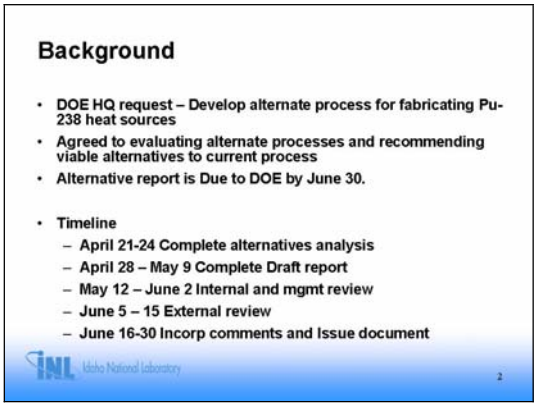
G-4. INTRODUCTORY REMARKS

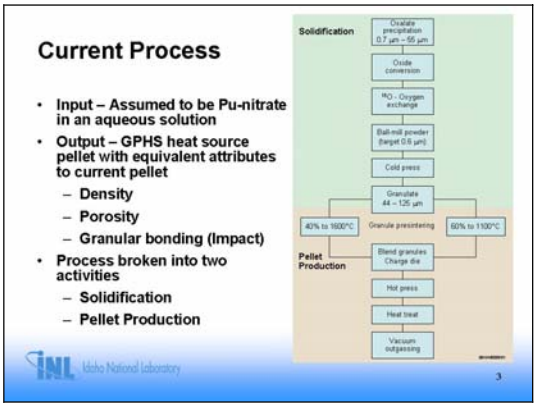
The workshop opened with comments from Steve Johnson, whose major points included:

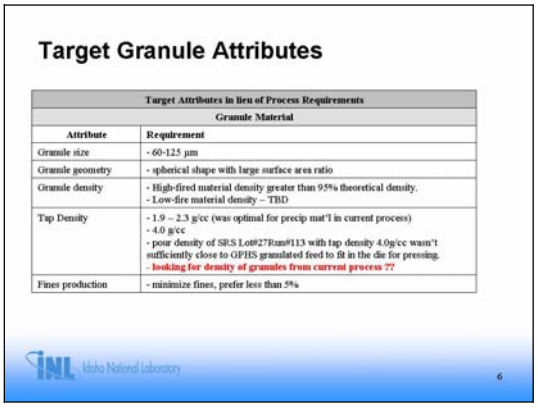
- The goal of this workshop is to examine the fabrication methods to make heat sources.
- The current process has been going on for three decades.
- The space program has gravitated to a single type of heat source that gives acceptable results for the safety analysis of the launch.
- However, preparation of the source leads to facility condition problems.
- The committee's task is to come up with a process that has advanced safety features for the worker and exhibits good performance for launch.
- 2006 is the last publication of the specifications document. It has only two clear product specifications; the rest of the document is process specifications.
- The goal is to have a different process for making the product that fits within the safety specification.
- The goal of this workshop is not to pick a single alternative, but use the criteria and preliminary screening to reduce the potential list of processes.
- Dennis Miotla at DOE is interested in the outcome of this effort.

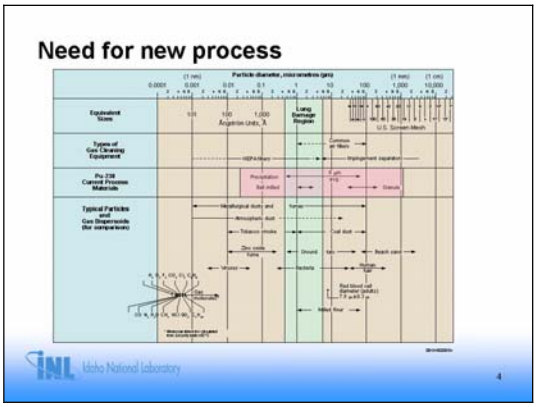
Linda Seward, facilitator, gave a review of the agenda and workshop objectives. Mark Borland, meeting lead, provided background information.

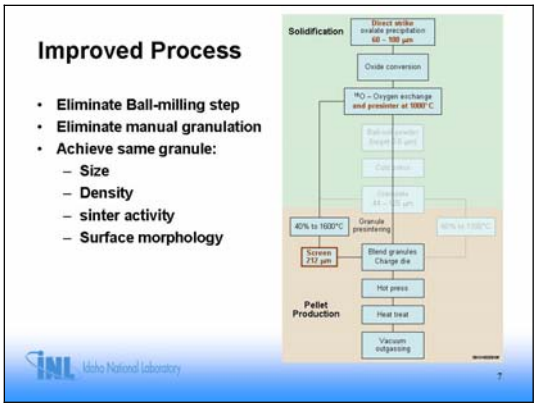


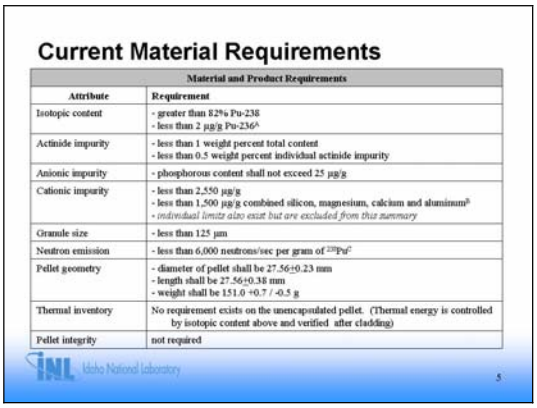




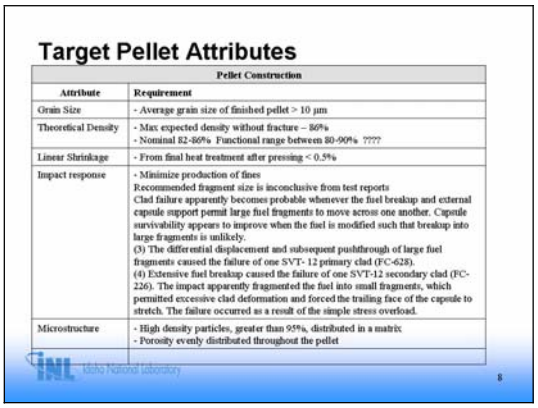








Material and Product Requirements	
Attribute	**Requirement**
Isotopic content	- greater than 82% Pu-238 - less than 2 µg/g Pu-236^
Actinide impurity	- less than 1 weight percent total content - less than 0.5 weight percent individual actinide impurity
Anionic impurity	- phosphorous content shall not exceed 25 µg/g
Cationic impurity	- less than 2,550 µg/g - less than 1,500 µg/g combined silicon, magnesium, calcium and aluminum[b] - individual limits also exist but are excluded from this summary
Granule size	- less than 125 µm
Neutron emission	- less than 6,000 neutrons/sec per gram of ^{238}Pu[c]
Pellet geometry	- diameter of pellet shall be 27.56±0.23 mm - length shall be 27.56±0.38 mm - weight shall be 151.0 +0.7 / -0.5 g
Thermal inventory	No requirement exists on the unencapsulated pellet. (Thermal energy is controlled by isotopic content above and verified after cladding)
Pellet integrity	not required



Pellet Construction	
Attribute	**Requirement**
Grain Size	- Average grain size of finished pellet > 10 µm
Theoretical Density	- Max expected density without fracture – 86% - Nominal 82-86% Functional range between 80-90% ????
Linear Shrinkage	- From final heat treatment after pressing < 0.5%
Impact response	- Minimize production of fines Recommended fragment size is inconclusive from test reports Clad failure apparently becomes probable whenever the fuel breakup and external capsule support permit large fuel fragments to move across one another. Capsule survivability appears to improve when the fuel is modified such that breakup into large fragments is unlikely. (3) The differential displacement and subsequent pushthrough of large fuel fragments caused the failure of one SVT- 12 primary clad (FC-628). (4) Extensive fuel breakup caused the failure of one SVT-12 secondary clad (FC-226). The impact apparently fragmented the fuel into small fragments, which permitted excessive clad deformation and forced the trailing face of the capsule to stretch. The failure occurred as a result of the simple stress overload.
Microstructure	- High density particles, greater than 95%, distributed in a matrix - Porosity evenly distributed throughout the pellet

General comments from Mark Borland's presentation included:

- A goal is to provide a DOE complex-wide perspective, a team effort, not just an INL product. This is a joint national lab product.
  - Question: Will there be a look at the integrated process because some of the alternatives from Parts A and B will go together better?
  - Answer: We will look at the combinations after we have down selected the parts. We will take time at the end of the meeting to discuss the integration aspects.
- The committee's charter is not to come up with a single solution, but to identify the best alternatives and to look at technologies to improve safety of the operation.
- Comment: Chemical purity should be added to the list of target granule attributes (Slide 3).
- The mission is to produce a granule with the specifications identified on Slide 6.
  - Question: How important is the maximum amount of silicon?
  - Answer: It is very important and a major contributor to pellet impurity.
  - Question: Is there an assumption that this process will be sufficiently different than the current product requiring a whole new qualification?
  - Answer: Not making that assumption. We will not know enough even after this meeting to make a conclusion.
- It is not in DOE's budget or vision to do a $40-50 M requalification of a new process.
- To tie the new process to the existing product, all characteristics of the existing product with statistical support is needed. This leap cannot be made without extensive characterization of the products.

- It should be accepted that some testing on the new product will be required.
- If the assumption is that the only specifications of concern are chemical purity and impact analysis and not the internal structure, this is a critical assumption.
  - Answer: Microstructure is a critical attribute of the design.
  - Question: What is the definition of fine powder size?
  - Answer: Less than 10 μm.
  - Question: Is this a product sufficiently different from the original product?
  - Answer: There is not enough information to make the judgment. Will need to test and make pellets and understand their behavior to determine if a minimum requalification is justified. LANL had a strategy to do a minimum requalification of about 10 pellets to qualify a change.
  - Question: The same process has been tried as used at LANL, but the results were not the same.
  - Answer: If changes are made to the current Pu-238 process or the facility location, additional minimum qualification tests or a political decision is required to qualify material for space flight.
  - Question: Something will have to be tested. The difference is running 5, 10 or 15 pellets. If the new process is very far away from the current process, can the tie back to the original process be made?
  - Answer: As long as the pellets break up in a similar manner, consider that the hydroxide precipitation process granules were different but acceptable.
  - Answer: The original development of the choice for all missions was a $40-50 M effort. DOE would not want to spend that amount to establish a new pellet.
  - Answer: Tasks may be simplified with good modeling techniques and far less testing.
  - Question: To tie to the existing product requires statistics. How can it be ensured the new process produces the same product?
  - Answer: A number of impact tests are necessary. The pellet should pass the impact test, for example, not break the cladding, meet the chemical purity requirements, and meet the source term requirements. Do not over constrain the requirements; the vents must be retained.
  - Question: Is the assumption that the microstructure is the same as the current microstructure?
  - Answer: It is purely process. Criteria like impurities and impact performance link to the same process as before.
  - Question: If copying the process and moving to a different site will require impact testing, should the hydroxide process be considered?
  - Answer: There is a wide range of microstructures between the hydroxide and oxalate processes. The final report will identify some alternatives based on the hydroxide process.
- The target product for discussion in the first part of this meeting will be a green granule.

G-5. ASSUMPTIONS

The following assumptions were agreed to by the committee:

- At some point there has to be a new source of Pu-238.
- Neptunium targets will be irradiated to produce Pu-238.
- There will be a very pure product going into heat source production.
- Chemical purity is sufficient for the feed going into heat source production.
- The pellet process will produce a single pellet of the right size (no cutting or grinding).

Current Oxalate Precipitate Process by Dennis Bickford

SRS $^{238}PuO_2$
Powder Production

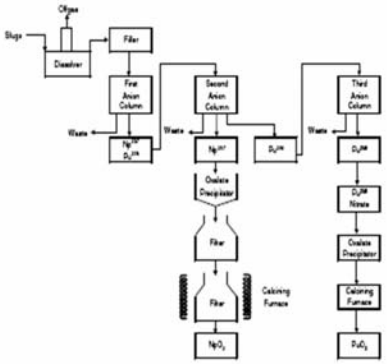
WSRC-MS-2000-00061 (U)
H.J. Groh, W.L. Poe, J.A. Porter

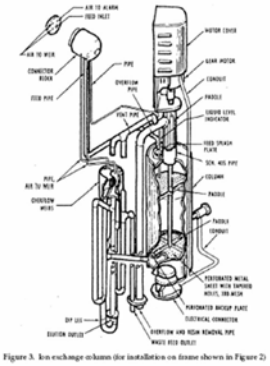
Precipitation and Conversion

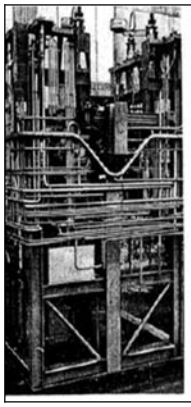
In the HB Line, the plutonium solution from H Canyon was processed by anion exchange, for decontamination and concentration. Then, the nitric acid concentration was adjusted within the range of 1-2M and plutonium valence was adjusted to (IV) by adding ascorbic acid and hydrazine nitrate and heating to 50°C.

Plutonium (IV) oxalate was precipitated at the same temperature by its addition to 1M oxalic acid solution. After digestion to aid crystal growth, the slurry was cooled to room temperature and filtered and air-dried.

Plutonium dioxide was produced by heating the plutonium oxalate in air to a final temperature of about 550°C.







SRS Np/Pu Remote
Separation Frame

Comments on the presentation as captured by the facilitators were:

- The pellet production process produces a 400 g/pellet batch at LANL.
- Production capacity required is 5 kg per year of finished product–need to produce 7-8 kg/year to accommodate losses.
- SRS stopped producing Pu when the reactor was shut down.
- SRS stopped precipitating Pu-238 about 5 years ago.
- There may have been some recycle after that.

- Some Russian material was brought in and purified.
- Chemical purity was the issue, not particle size.
- The product looked like carpenters' pencils, jack straw sort of things with low-density powder not conducive to pressing into a pellet. That was the reason for ball milling. Process variation caused disruption for LANL.
- Shortcomings of the HB-line precipitator were large hurdles. It is easily controlled for chemical purity, not for optimization of particle size.

Improved Oxalate Precipitate by Dennis Bickford

Direct Fabrication of Oxalate Precipitated $Pu^{238}O_2$

DP-1621 (U)

G.A. Burney & J.W. Congdon

Flowsheet for Direct-Strike Pu(III) Oxalate Precipitation (Two-Step)

1. Feed Adjustment
   - 1.2 ±0.2M HNO_3
   - 5 ±2 g Pu/L
   - 0.05M $N_2H_5NO_3$
   - 0.05M Ascorbic Acid
2. Transfer Adjusted Feed to Precipitator

The current process for the fabrication of $^{238}PuO_2$ heat sources includes precipitation of small particle plutonium oxalate crystals (4 to 6 µm diameter), calcination to PuO_2, ball milling, cold pressing, granulation (60 to 125 µm), and granule sintering prior to hot pressing the fuel pellet.

A new two-step direct-strike Pu(III) oxalate precipitation method which yields mainly large well-developed rosettes (50 to 100 µm diameter) has been demonstrated in the laboratory and in the plant. These large rosettes are formed by agglomeration of small (2 to 4 µm) crystals, and after calcining and sintering, were directly hot pressed into fuel forms, thus eliminating several of the powder conditioning steps.

Conditions for direct hot pressing of the large heat-treated rosettes were determined and a full-scale General Purpose Heat Source pellet was fabricated. The pellet had the desired granule-type microstructure to provide dimensional stability at high temperature.

3. Oxalic Acid Addition to Precipitator

   23° ±3°C

   Oxalic Acid Adjustment No. 1 to $\frac{[H_2C_2O_4]}{[H^+]^3} = 0.011 \pm 0.002$
   (Addition Time 10 Minutes)

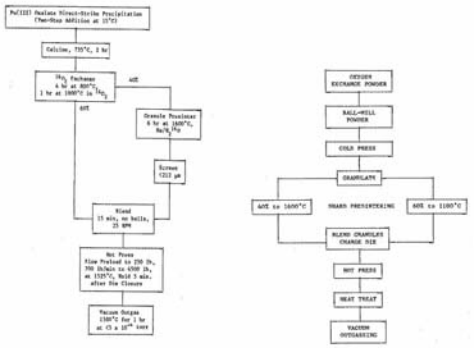
   Digest for 20 Minutes with Mixing

   Oxalic Acid Adjustment No. 2 to 0.22 ±0.02M Oxalate in Supernate (Addition Time 20 Minutes)

   Mix 5 minutes (After Oxalic Acid Addition Complete)

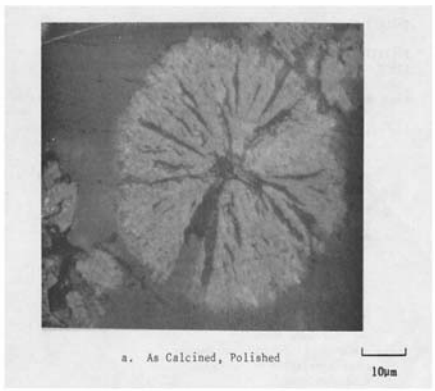
4. Filter
5. Wash the Pu oxalate with three cake volumes of 1.5M HNO_3 - 0.3M $H_2C_2O_4$ - 0.1M hydrazine - 0.1M ascorbic acid
6. Calcine the Pu oxalate at 650°C ±50° for two hours in air

Direct Fab. vs. Normal LANL / SRS Flowsheet

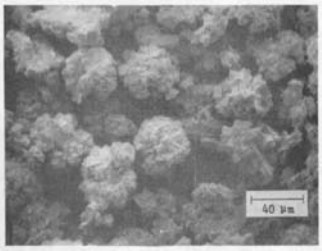


Precipitator Requirements:
a Nucleation and Growth Phenomenon

- Control # of Nuclei & Growth: minimum fracture
- Temperature control of reagents & reactor
- Reagent addition rate control
- Moderate but thorough agitation
- Good particle suspension
- Minimum heals / maximum flush out
- Smooth interior / no dead spots
- No chemical contaminants / residues

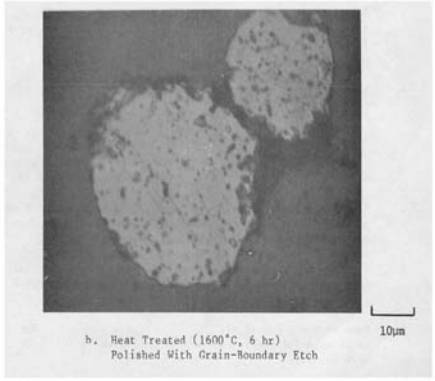


a. As Calcined, Polished

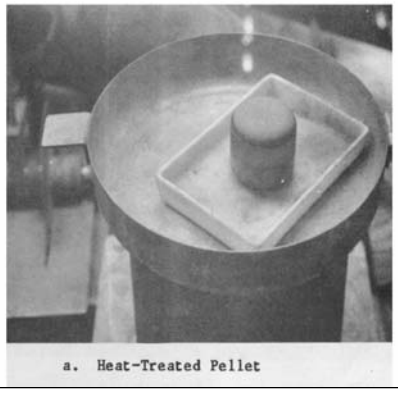


Run No. 203-HA-250

FIGURE 23. Pu(III) Direct-Strike Feed Produced in HB-Line by Two-Step Precipitation Method



b. Heat Treated (1600°C, 6 hr) Polished With Grain-Boundary Etch



a. Heat-Treated Pellet

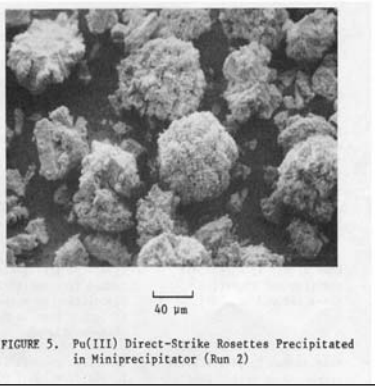
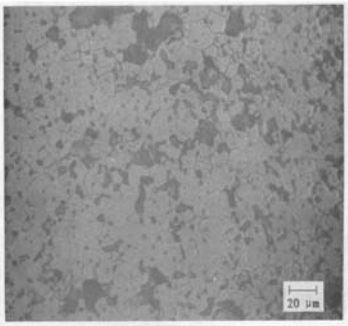


FIGURE 5. Pu(III) Direct-Strike Rosettes Precipitated in Miniprecipitator (Run 2)



Microstructure (Grain-Boundary Etch)

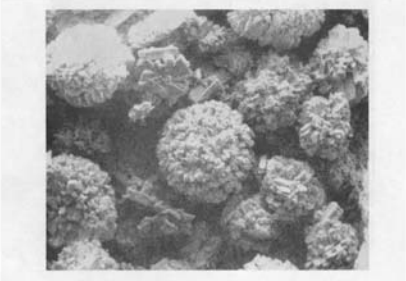


FIGURE 13. Pu(III) Direct-Strike Rosettes (15°C) (Addition and Digestion Times Doubled)

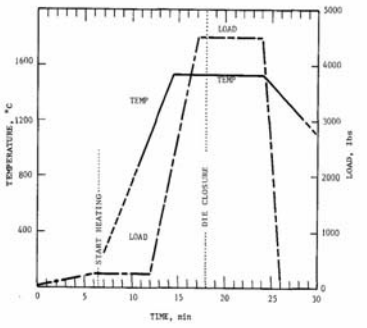
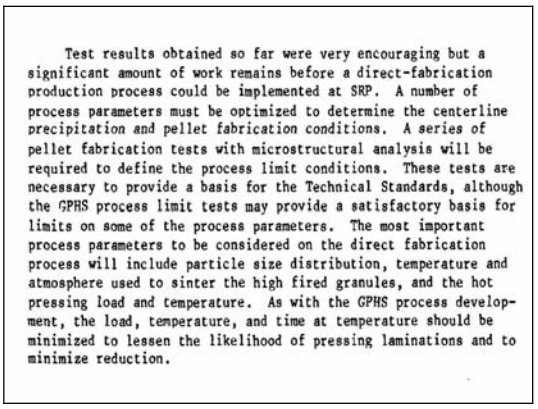


FIGURE 27. Direct Fabrication Hot Pressing Parameters

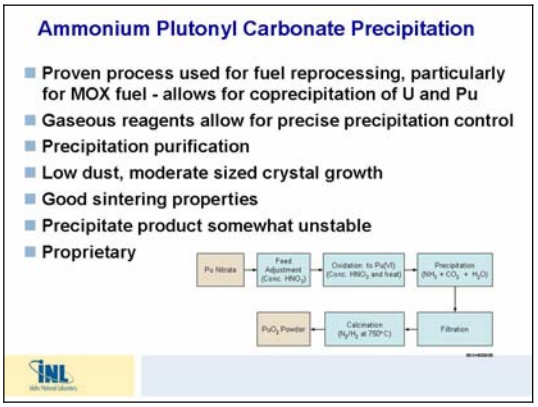


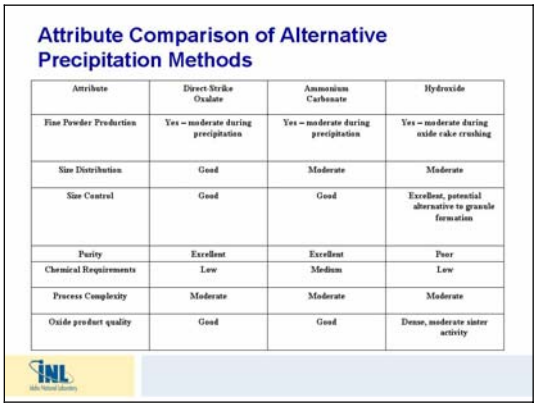
Test results obtained so far were very encouraging but a significant amount of work remains before a direct-fabrication production process could be implemented at SRP. A number of process parameters must be optimized to determine the centerline precipitation and pellet fabrication conditions. A series of pellet fabrication tests with microstructural analysis will be required to define the process limit conditions. These tests are necessary to provide a basis for the Technical Standards, although the GPHS process limit tests may provide a satisfactory basis for limits on some of the process parameters. The most important process parameters to be considered on the direct fabrication process will include particle size distribution, temperature and atmosphere used to sinter the high fired granules, and the hot pressing load and temperature. As with the GPHS process development, the load, temperature, and time at temperature should be minimized to lessen the likelihood of pressing laminations and to minimize reduction.

Comments as captured by the facilitators were:

- Direct strike Pu (III) oxalate precipitation method is the recommended method by SRS.
- Hand operations are used for moving powder.
- Research carried through to demonstrating full-size pellets.
- First batches were done with Pu-240, but then used Pu-238.
- The improved oxalate precipitation process was demonstrated in a precipitator that was not optimized.
- Calcine, oxidation, and sintering could be done in one step. Sintering accomplishes 95% density.
- Process minimizes production and transfer of powder and fines.
- Process reduces hand doses, entrainment, and simplifies facility.
- SRS did not build a new precipitator that was optimized for the improved process.
- High-fired particles (sintered at high temperatures) are the brick, and low-fired particles (sintered at low temperatures) are the mortar or binding.
- Vary the density of the particles by tailoring the mix to optimize tap, pour, and packing densities.
- SRS produced about four pellets.
- The objective of the pellet design is to achieve 82% theoretical density with porosity to keep the pellet dimensionally stable.
- Nominal particle size would be above the respiration range.
- Primary advantage in terms of fines is there is less handling of the powder.
- The same chemical purity can be achieved without running ball mills, purer than the normal product would be. Less chance of anything getting into it.
- There are decreased hand doses and risk to the operator, because granules come right out of the calciner, then move by boat with less handling.
- A problem at the PUFF facility was having cells with powder spread around, and no way to clean it.
- New process minimizes the size of facility, radiological dose, and opportunities for dispersion release.
- Grinding and then dumping material creates fines. These fines coat and stick to things, making it difficult to clean and leaving residue.
- If precipitator could be redesigned and have the optimum configuration, all heat treatments could be done in the same furnace and the only move is to go to batching and blend particles. Right processing temperature may allow one thermal treatment.

Carbonate Precipitate by Steve Frank

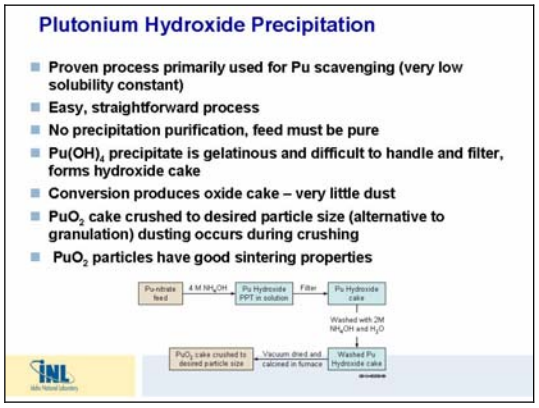


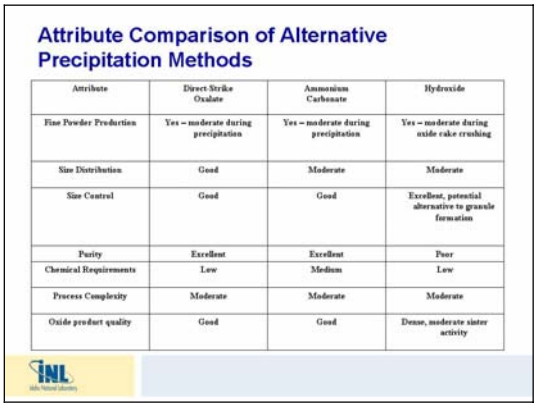


Comments as captured by the facilitators were:

- Precipitate product is somewhat unstable process; needs to be proven.
- Miniscule amounts of ammonium nitrate were introduced that caused all kinds of problems.
- There is very little experience with this process in the U.S.
- It results in a nice ceramic.
- It must be proven that the hydrogen is not reducing the Pu oxide.
- Process does not need the hydrogen reduction, just calcine.
- Advantage for developers is recycling of chemicals, very little waste production.
- Process patents are no longer protected.
- Timing of feed adjustment step is critical. When you oxidize the Pu, it will slowly revert from +6 to +4 valence (in 36 to 48 hours).
- When moving from small to big pellets, there are differences.
- It is hard to find published data on Pu work.
  - The information exists with ALCHEM but has not been made available.
- Process is based on uranium, and some Pu may not react the same as pure Pu. Need to demonstrate it can be done on actual Pu.

Hydroxide Precipitate by Steve Frank

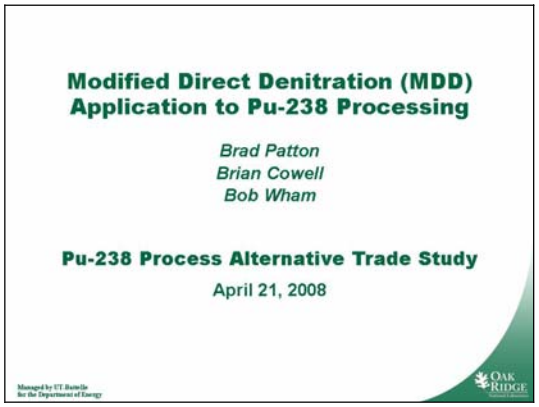


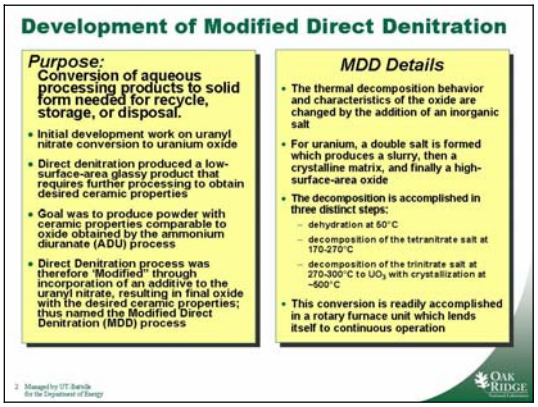


Comments as captured by the facilitators were:

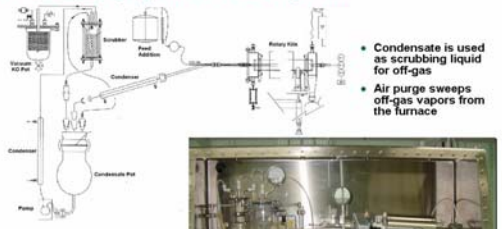
- There is an issue with the amount of throughput, owing to filtering and washing times.
- This process comes from the Savannah River proposal.
- Mound did the process, SRS proposed doing it.
- ALCHEM built a unit and demonstrated the process.
- Will have to do a valance adjustment.
- Must determine where crushing will be done.
- The precipitate does not crush up in round spheres, resulting in different shaped particles.
- Issue of ammonium nitrate may need to be addressed.

MDD-Denitration to Oxide by Brad Patton





Process Equipment Description

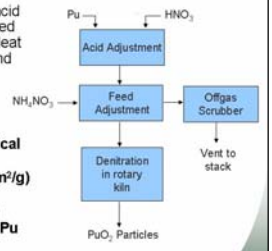


- Condensate is used as scrubbing liquid for off-gas
- Air purge sweeps off-gas vapors from the furnace

- Heart of MDD process equipment is the rotary furnace
- Metal nitrate feed solution enters furnace and exits as converted oxide powder

Direct Denitration (MDD) Application to PuO_2 Production

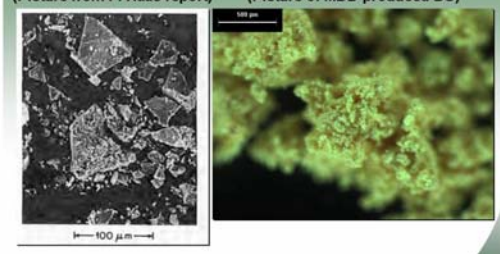
- ***Description*** - Starting with a nitric acid solution containing Pu, adjust the feed with ammonium nitrate (NH_4NO_3). Heat the solution to decompose nitrate and ammonia, leaving PuO_2.
- ***Potential Advantages***
  - High surface area per unit weight
  - Density of ~84–93% of theoretical density
  - Good ceramic activity (~5–15 m^2/g)
- ***Potential Disadvantages***
  - Work has focused on uranium denitration, very little work on Pu denitration
  - Not a dust-free product



MDD Runs With Depleted Uranium

Traditional Direct Denitration (Picture from P. Haas report)

Modified Direct Denitration (Picture of MDD-produced DU)



Simple Decomposition of Intermediate Salt Leads to Full Oxide Plus Gaseous Byproducts

Uranium conversion in MDD:

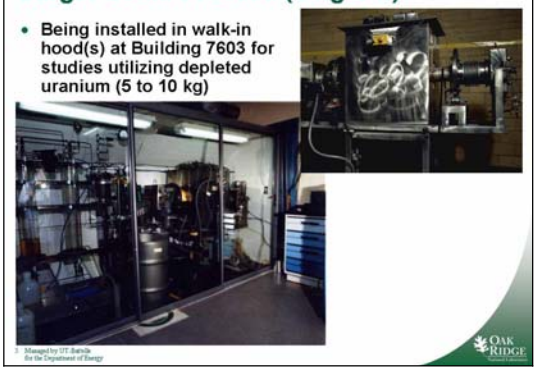
$$2NH_4NO_3 + UO_2(NO_3)_2 \rightarrow (NH_4)_2UO_2(NO_3)_4 \rightarrow UO_3 + 2NO_2 + 0.5O_2 + 4H_2O + 2N_2O$$

So, for Plutonium

$$2NH_4NO_3 + Pu(NO_3)_4 \rightarrow (NH_4)_2Pu(NO_3)_6 \rightarrow PuO_2 + 2N_2O + 4H_2O + 4NO_2 + O_2$$

Larger Scale Process (1 kg U/h)

- Being installed in walk-in hood(s) at Building 7603 for studies utilizing depleted uranium (5 to 10 kg)



MDD Pu Conversions

- Cold testing with cerium
- Plutonium Conversion
- MDD Co-conversions
  - U/Pu- 90 wt% U and 10 wt% Pu
  - U/Pu/Np ratios of 90.4/9.1/0.5 wt% respectively
    - Fraction in condensate ~0.5% of feed
  - U/Pu/Np/Am ratios of 92.3/ 7.15/ 0.31/ 0.28 wt% respectively
    - Fraction in condensate were 1.0 % Np/ 1.1% Pu/ 0.2% Am respectively
  - Recycle-condensate from all co-conversion runs was collected
    - Ammonium hydroxide precipitation
    - Decanted solids and fed as slurry

MDD DU Powder Characterization

Calcination/reduction and sinterability studies

- Run 062507
- Run 062707- produced at higher temperature, some U_3O_8 present before calcination/reduction

Powder	Calcination/ Reduction	Surface Area	Green Pellet	Sintered Pellet
062507	Dry 4% H_2/Ar	3.0 m^2/g	49% TD	95% TD
	Moist 4% H_2/Ar	2.2 m^2/g	51% TD	91% TD
062707	Dry 4% H_2/Ar	1.8 m^2/g	54% TD	92% TD
	Moist 4% H_2/Ar	1.6 m^2/g	56% TD	90% TD

Milling of powders before pressing was found to lower sintered densities.

MDD Conversions

Plutonium Conversion

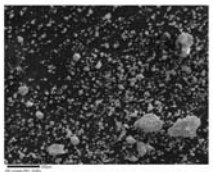
- First "hot" tests with plutonium nitrate solutions- operationally successful
- Operating conditions used were developed during cerium testing
- Product inherently flowable

Uranium Conversion

- Typical Op Conditions:
  Feed – ~200 g/L U
  Rate – 5 mL/min
  Furnace Temp – 675°C
  Tube Rotation – 34 rpm
  Incline – 6.5°
  Purge – 0.3 cfm
- Typical uranium oxide tap density: 1.1 – 1.2 g/cm^3
- Fraction in condensate ~1%

MDD-PuO_2 Product Characteristics

- Bulk density: 2.2 g/mL
- Tap density: 3.0 g/mL
- Particle size:



SEM photograph of a sample of plutonium dioxide MDD product

Particle size, µm	Weight %		
	Sample P01 (SEM)	Sample P02 (SEM)	Cerium run (sieved)
≥710	29	26	37
180	57	52	40
75	7	9	14
≤ 38	7	13	9

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MDD Powder Characterization (cont.)

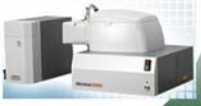
Equipment installation and testing in glove boxes is on-going

Powder Rheometer

XRD

BET Surface Area Analyzer

Calcination/ Reduction Furnace



Laser-light Particle Size Analyzer

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Pellet Fabrication–Test CeO_2 Pellets

- CeO_2 from earlier MDD runs
- Uniaxial hydraulic press

Variables- calcination/sintering conditions, binders, pressing pressure, powder, slugging, L/D

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Advantages of MDD Process for Application to Pu-238 Processing

- Produces a free-flowing product which can be directly pressed into a pellet
- Chemistry and uranium oxide product characteristics are well understood (1980-present)
- Development underway by GNEP for actinide conversion (operating conditions and product characterization)

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Further Work Required for Application to Pu-238

- Optimize MDD operating parameters for PuO_2 production
- Characterize products
- Press test pellets and examine
- Sinter pellets and examine
- Plans for GNEP to install pellet fabrication, sintering, and examination equipment (equipment and gloveboxes are procured) for MDD plutonium product characterization

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Disadvantages of MDD Process for Application to Pu-238 Processing

- May not achieve any reduction in dusting relative to reference ex-oxalate powder
- Most work to date with uranium

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MDD Powder Characterization

Four new glove boxes have been received and glove box approvals and equipment testing are progressing

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Comments as captured by the facilitators were:

- Dissolving Pu oxide is more difficult than ammonium hydroxide. Would need a dissolution step for bulk product.
- Discussion on comments from team members included:
  - There is limited experience with Pu oxide.
  - MDD is not a dust-free process.
  - This is similar to oxalate; potential for small particles if agglomerates get broken up. Kiln breaks up the agglomerate. Small particles will exist in the MDD process.
  - Granules from the MDD process are difficult to characterize.
  - ORNL's experience shows it is a repeatable process.
  - Applies to all agglomerates of small particle size. Handling results in respirable fines.

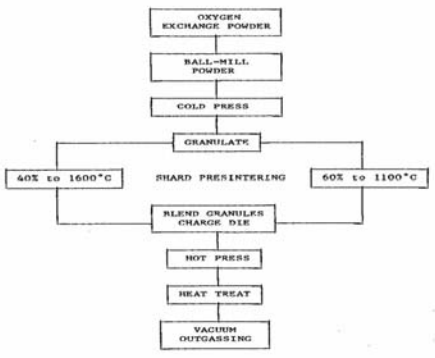
Current Granulation Process by Dennis Bickford

Heat Source
Oxalate Based Flow Sheet

LA 7972 MS, R.A. Kent
DPST-80-00128-002 (U)

Outgas

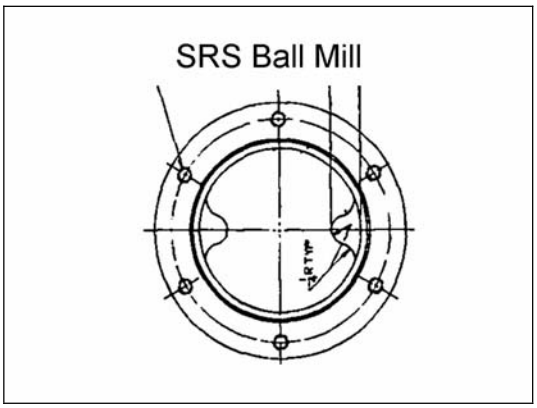
Heating the powder for 1 hr at 1000 ^{0}C, a temperature higher than the calcining and oxygen exchange temperatures, normalizes the powder to the same thermal history and also frees stored decay helium. Normally, the outgas and ^{16}0 exchange operations are performed in the same heating cycle.

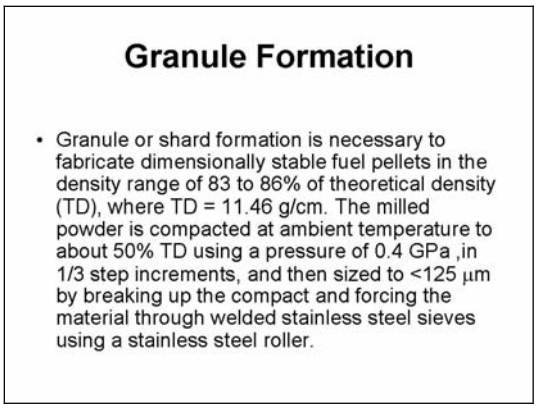


Milling

Dry milling for 12 hr at 100 rpm in hardened stainless steel mills with hardened stainless steel balls grinds the elongated lathe-shape feed particles of nominally 5 μm to a more uniform shape and uniform size of -1.4 μm.

LANL used unbaffled mills at lower rpm for longer.

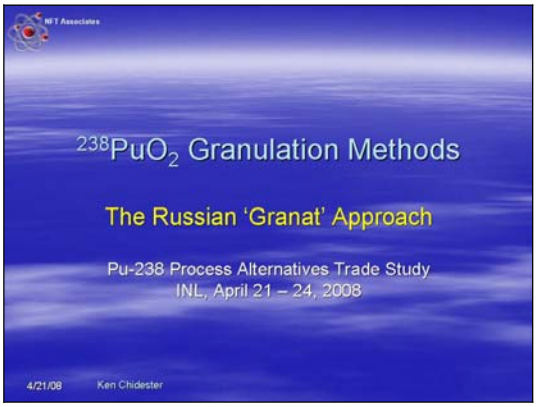


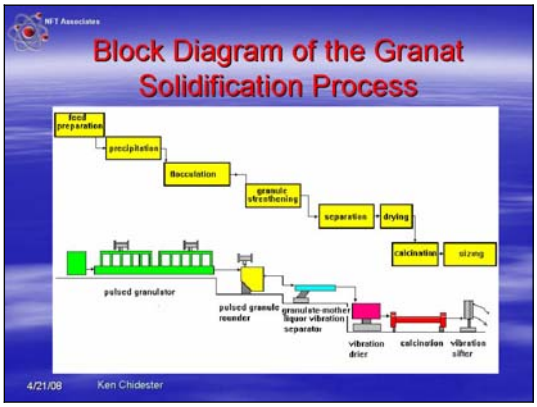


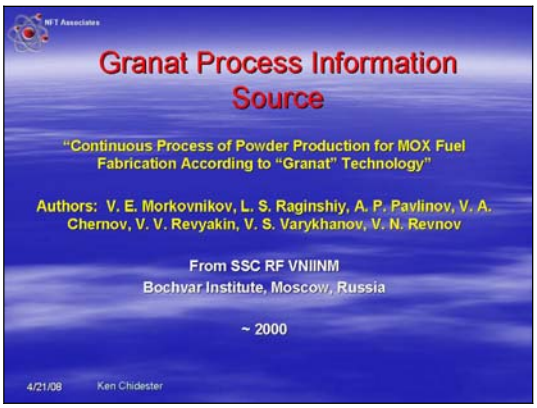
Comments as captured by the facilitators were:

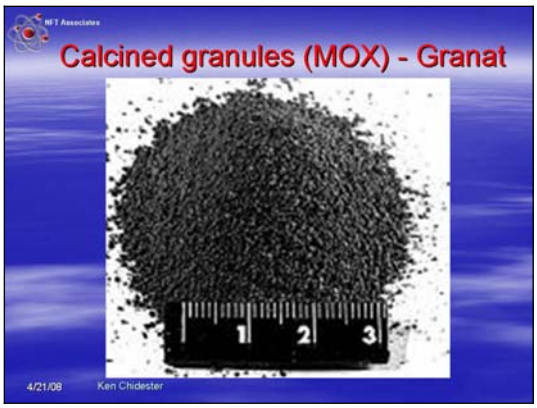
- Process control issues are: sensitivity to temperature gradients in the furnace, can get up to 100-degree variation owing to self heat.
- Granulation and transfers are performed by hand.
- It's hard to characterize the granular product and prove consistency.
- Screened and loaded granule material onto furnace trays in 75-g batches, 450 g per furnace batch. Batches were loaded into vertical tube furnaces.
- Discussion of comments from team members included:
  - Remote methods exist for granulation.
  - Tom Wheeler is looking at remote methods in the improved equipment section of the report.

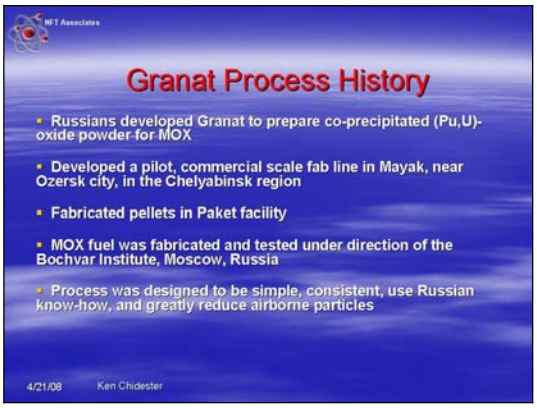
Russian Approach (Flocculation) by Ken Chidester

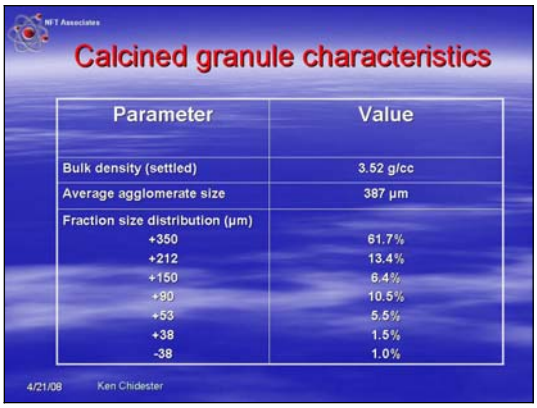


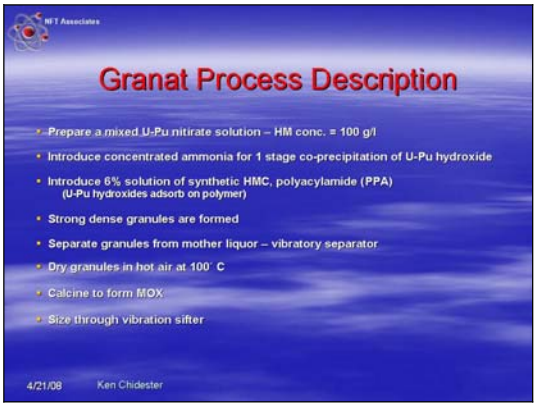










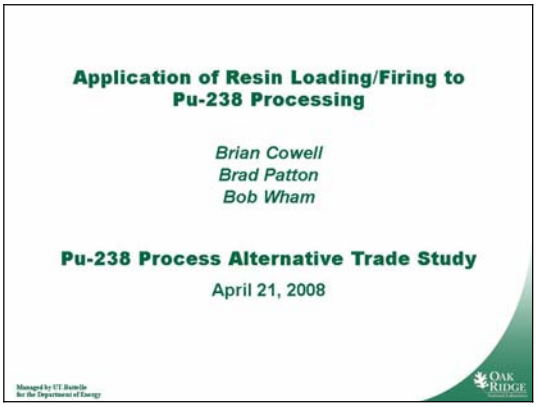


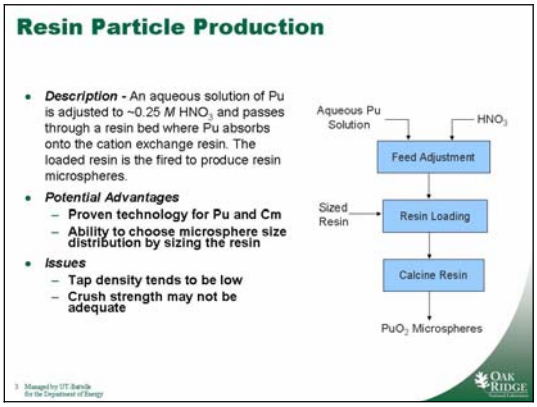
Comments as captured by the facilitators were:

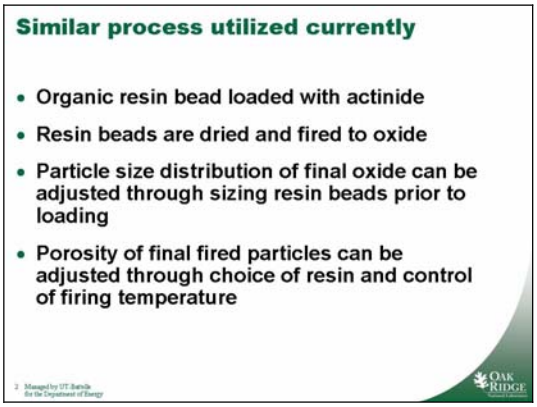
- Approach was successful in taking material from precipitation to pellets for MOX.
- Total impurities would be <1500 PPM.
- There are less than 1% fines. Continuous process automated temperature control and flow of material. This results in uniform, flowable material. Material does not easily come apart. Met the MOX specification for impurities.
- Surface morphology is rosettes.
- Is it appropriate to use binders for particle formation before heat pressing?

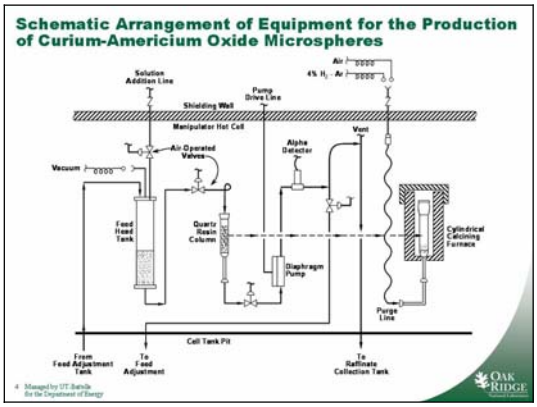
- Precipitating agent is ammonia.
- Will the organic stand up to the heat and alpha radiation without breaking down?
- Produces a ceramic material that is easy to work with, gets rid of the fines.
- Discussion of comments from team members included:
  - Organic additive could be used in other precipitation processes. Gets rid of concerns for hydroxide process.
  - May be able to obtain material from Mayek pilot facility in Russia. Could find out their experience with pure Pu.

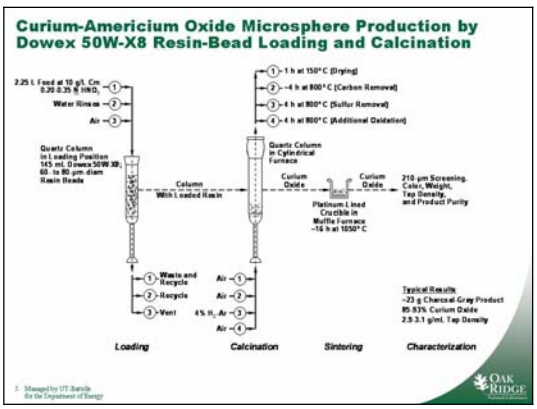
Resin Particulate Production by Brian Cowell

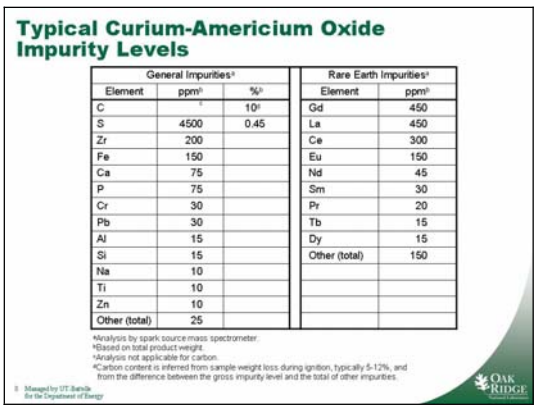






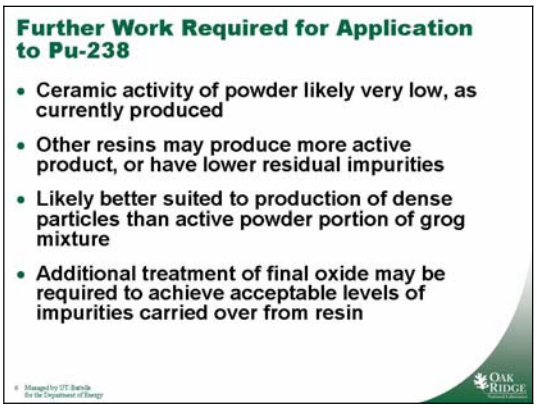


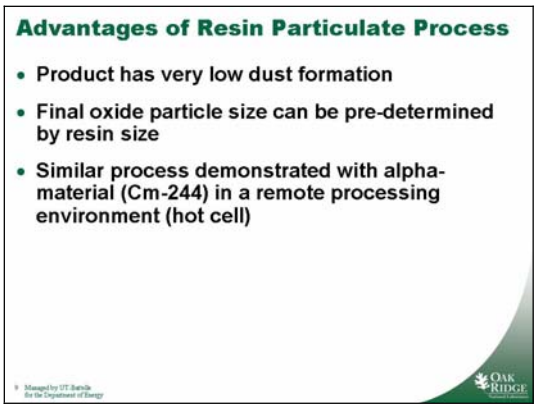


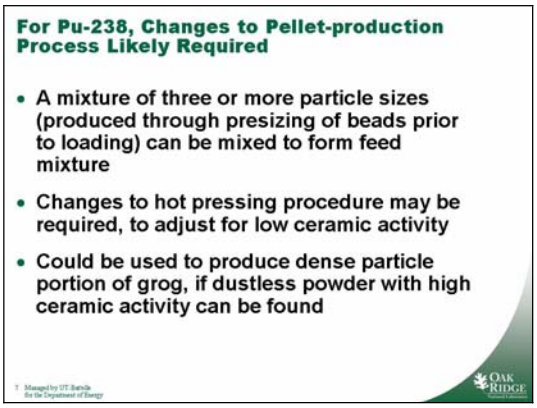


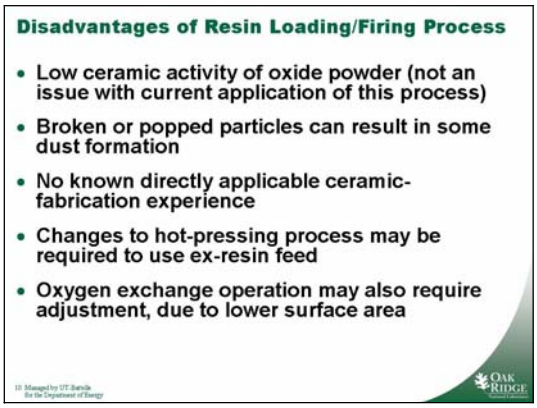
General Impurities[a]			Rare Earth Impurities[a]	
Element	ppm[b]	%[b]	Element	ppm[b]
C		10[c]	Gd	450
S	4500	0.45	La	450
Zr	200		Ce	300
Fe	150		Eu	150
Ca	75		Nd	45
P	75		Sm	30
Cr	30		Pr	20
Pb	30		Tb	15
Al	15		Dy	15
Si	15		Other (total)	150
Na	10			
Ti	10			
Zn	10			
Other (total)	25			

[a]Analysis by spark source mass spectrometer.
[b]Based on total product weight.
[c]Analysis not applicable for carbon.
[d]Carbon content is inferred from sample weight loss during ignition, typically 5-12%, and from the difference between the gross impurity level and the total of other impurities.





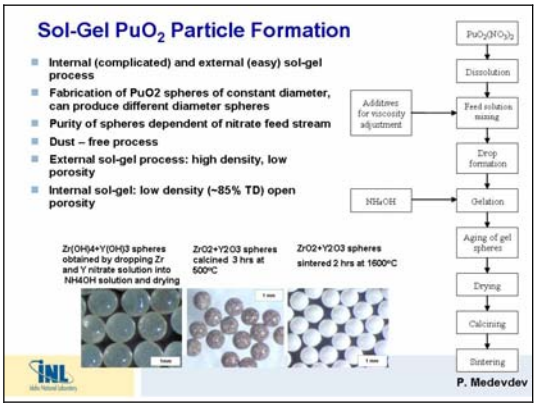


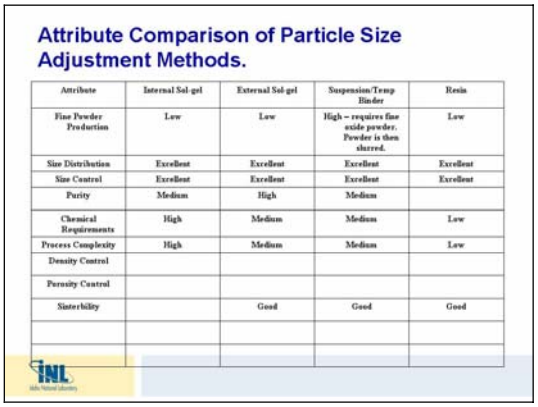


Comments as captured by the facilitators were:

- Porosity may be an issue. Control the porosity with choice of resin and firing process.
- Not proven for Pu-238 applications. Sulfur impurities may be an issue.
- This process is not optimized for Pu-238. It is basically dust free and the size can be controlled. It has been demonstrated in a remote environment.
- If the process were stopped at a lower temperature, would you get a better formation?
- The process cuts out a lot of steps, close relative of gellation. Has worked with high alpha materials.
- There are a limited number of choices for resin beds.
- Discussion of comments from team members included:
  - Impact of Pu-238 on the process—has more alpha and less gamma.
  - Process has experienced high alpha load (curium) on sulfonated resin
  - Carboxolated resin will be more sensitive to radiology than sulfur. Issue can be worked out.
  - Quantities/throughput—Can it scale up?
    - Answer: There is no scale limitation on the process.
  - Flow hydrogen in an argon carrier to get the salts out. Residual carbon adds moisture to slow down the oxidation. Would not have to dry a whole column before combustion.

Sol-Gel Particulate Production by Steve Frank

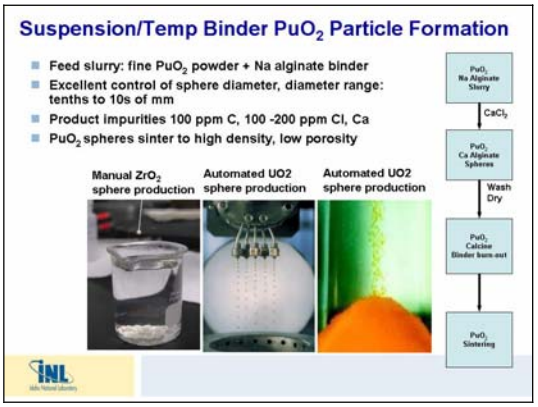


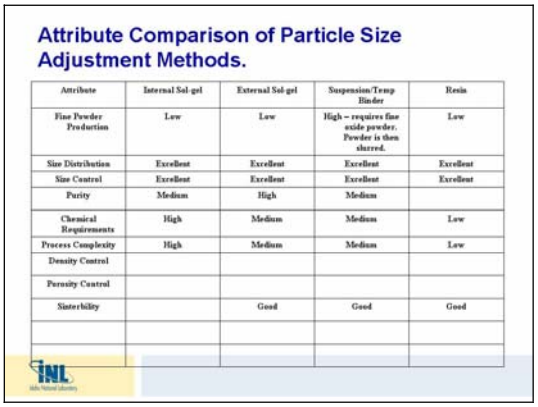


Comments as captured by the facilitators were:

- Process is scalable and automated.
- Makes totally spherical particles. Particles can be tailored.
- Process involves high risk and investment.
- Can this process be used with a hot press?
- Does it have sinterability and hot press ability?

Spherizator Particulate Production by Steve Franks



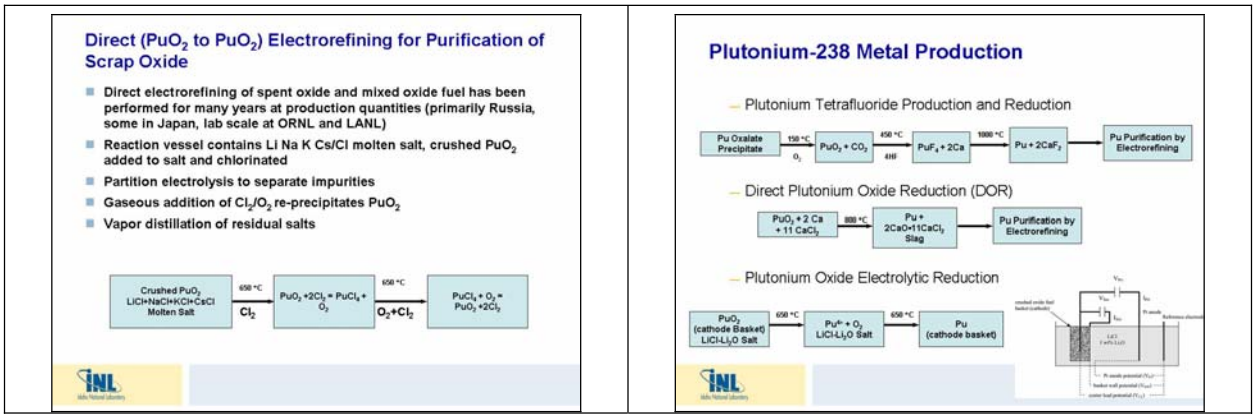


Comments as captured by the facilitators were:

- A lot of unanswered questions remain with regard to use of Pu-238.
- Will have a hard time proving that the process will get all the impurity out.
- It gets high density required. Can produce very high density product.
- It is more benign than Sol-Gel.

Pyro Electrorefining (New Alternative) by Steve Frank

Brian Cowell proposed an additional alternative for Pyro Electrical Chemical Processing. Steve Frank presented slides on the process. Because of the assumption of a nitrate feed, this alternative does not fit and will not be considered further.



Comments as captured by the facilitators were:

- There is information available on this process.
- Material as currently used is vibration compaction that generates 80% bulk density and it is stable.
- The outer portion never restructures at its temperature. Material is left as a category for scrap recycling of UO_2 or PuO_2.
- There is little information on ceramic possibilities. Russian and Japanese sources may have additional information.
- Attempted to make pellets but had to ball mill excessively. Same as to handle scrap.
- If a hot press method is used, it will fracture in the granules that are formed.
- Shards are randomly sized. Information on the microstructure is obtained by vibration.
- Must figure out how to make in sinter.
- Sounds complicated for a small operation.
- Can do in small batchers. With MOX, small batch sizes can be run.
- Claimed to be a dust-free process.
- If there were a capability to cold test, it would be interesting to see if the material would bond together.
- Looking at it for a different project—scrap recycling.
- Some aspects of this alternative are significantly different than the standard precipitation approach. The concept is simple, requiring little handling in hot cells and gloveboxes. Information is available on the process chemistry and final pellets.
- It's done in Russia. LANL did on a small scale.
- Typical cycle time, including getting rid of residuals, is about 48 hours/batch.
- Is limited by material, not scale.

- There are radiation issues, because of alpha with the salts.
- Developed for a closed fuel cycle that is proliferation resistant.
- Set up to run remotely.
- Used for metals to get good purification.
- PuO_2 coming out looks like the inside of a geode. Porous, not solid.
- Very granular. Free flowing, does not look like powder.
- Chlorine is removed.
- What are the volumes of residual salts?
  - Do not know.
  - We do salt clean up and get low levels.
- Needs an oxide conversion.
- Need to separate neptunium from Pu.
- Initial dissolution to get to granules. Fission products still remaining, need chemistry separations.
- Process provides separation, but not as good as acid.
- Would have to do multiple refinement steps.
- Can the salt be dried and then dissolved?
- Needs a step to dry or precipitate to get feed stock for the furnace.
- Separate and get a crystalline structure and then must drive off chloride.
- Must crush the material to get a granule.
- Four-step operation.
- Is a sintering operation needed for the granules?
  - Answer: No. The granules are ready to go when they are the right size. Hot pressing at temperature and pressure would form granules.
- Starting with a nitrate solution and feed salts.
- Can buy from Russia an oxide that will feed into the process.
- Assumption is the process is starting with nitrate. If this assumption cannot be changed on the feed, this is a potential problem.

G-6. PROCESS INTERROGATION DISCUSSION

The committee discussed the need for real-time process interrogation. The goal is to be able to interrogate the process as it is going for quality control.

- Quality control measures are affected by heat.
- Fine particle size may result in
  - Sediment
  - False readings.

Could a laser be used to measure these issues?

- Granules porosity is important:
  - Mercury porosity
  - Measure particle infiltration
  - Particle measurements.
- May be able to answer some of the questions with computer simulation or computer measurement systems.
- Precipitator will be built as described by Dennis Bickford.
- Granule quality. Conduct a hot press as a control sample.
- Remediation may be a quick recycle before pellet formation.
- Start up is limited by the availability of powder.

G-6.1 Participant Comments on Alternatives Before Scoring

Committee members, working on computers, commented on each of the alternatives without interpretation or transcribing by facilitators.

1. Current Oxalate Precipitate Process
   - Process has given product that works with hot pressing for final densification.
   - There is a long history of success using the process.
   - It is the only flight-qualified process at this time.
   - There is a problem with dust during milling and slugging operations. With respect to this comment, could enclose processing within the gloveboxes address release of dust during milling and slugging?
   - There is a lack of end-product specifications.
   - There is a need to characterize products and stream to the extent possible to help guide the development of the improved process. There is a lack of characterization parameters (e.g., porosity) for granules.
   - Granulation steps are difficult to characterize for process control.
   - Process requires too many hands-on operations. With respect to this comment, could the process be automated and enclosed or otherwise isolated from the glovebox interior atmosphere?
   - The ball milling of the precipitate produces respirable fines that have resulted in significant dose during accidents in the process lines.
2. Improved Oxalate Precipitate
   - Pellets were made with this process.
   - There still appears to be too many fines produced.
   - Good process. Directly forms large granules that can be fired. Eliminates a lot of handling and dust problems found with the current process.
   - Still requires multi-step processing with potential fines.
   - Pellets made with this process were not impact tested.
   - From the perspective of releasing fines, what is the potential for automating and enclosing this process?
   - Filtration and precipitate handling has potential to generate fines.

- It is the only alternative demonstrated at full scale with Pu-238.
- It is the only alternative with both centerline and process limits demonstrated.
- Shape of granule is still not spherical.
- There is an incremental improvement in the process. Other approaches may yield more significant process improvement.

3. Hydroxide Precipitate

- Does not appear to be any advantage over the improved oxalate precipitation process.
- Seemed to work for Mound Laboratory, so must be seriously considered.
- Process produces different-shaped particles than oxalate process.
- It is one of only two processes that has been flight qualified (multi-hundred watt).
- Process demonstrated to have fewer fines and safety issues than normal process.
- Could represent one extreme of acceptable microstructures as compared to normal process.

4. Carbonate Precipitate

- There is not enough information to say if it is better that oxalate processes.
- Seems similar to other precipitation, but less proven for this case.
- There is a lack of U.S. experience with the process, and it does not appear to have advantages over improved oxalate process.

5. MDD-Denitration to Oxide

- It is a simple one-step process.
- Is there experience with Pu oxide?
- Is there a way to control agglomerate size?
- It is cost-effective. Simple process.
- It is not a dust-free product.
- It is a serious candidate.
- Other programs interested in developing process, which should result in some shared costs.
- Product difficult to characterize. Not demonstrated for any similar Pu/porosity product.
- There is a large technical investment/risk.
- Process appears to be very compact.
- Corrosive nature of Pu-238 incompatible with rotary kiln.

6. Current Granulation Process

- The portion of 1100°C granules versus 1600°C granules may not be correct. It seems that for good packing of 1600°C granules, fewer of the binding granules are needed. This could be studied with surrogate materials.
- Need to consider granulation for all powder processes in broad context. Digestion/aging of the precipitates is granulation in a broad sense. Some low-dusting and remote (not hands-on) granulation methods exist and should be considered.
- Current granulation process creates a bunch of fines/dust.
- There is not a lot of control to this process. Hand worked.
- This is only flight qualified process for GPHS.

7. Russian Approach (Flocculation)
   - No U.S. experience with the process is a concern.
   - It was developed for U/Pu oxides. Will it work with 238 Pu only? It forms flowable powder with no fines.
   - Process produces very few fines.
   - I like this approach because it eliminates fines and could be used with other techniques. I also noted in the original paper that the size of the granules could be adjusted during the drying process by the vibration and rate of flow of warm air. This is almost like a fluidized bed. My interest is in fabricating the pellet.
   - This can be used as feed to either cold press and sinter or hot press, but needs process testing.
   - Makes some nice, big, round, granules.
   - There are worries about heat and radiation of 238PuO2 causing trouble with the organic flocculation chemicals.
   - Process is not significantly better than oxalate, and less proven.
   - Organic additive could be used in other precipitation processes.
   - The U.S. has no experience with the process.
8. Resin Particulate Production
   - It is unclear if the large carbon contaminant is an issue for the final product.
   - There is concern regarding firing operation of resin. It has acceptability from emissions and safety basis.
   - It is not clear what impact Pu-238 will have on this process.
   - It has some potential, but we need more information.
   - We need to understand what granules look like if calcined to about 600-700 °C.
   - There is a high technical cost and risk to qualify.
   - There is a need to determine other impurity levels.
   - It was demonstrated in high alpha environment with high decay heat materials.
   - It offers few steps and easiest control of granule morphology. Can sulfur be removed by proper gas/temperature treatment? This could be learned in surrogate study.
   - What about throughput?
9. Sol-Gel Particulate Production
   - Heat from Pu-238 may affect the gelation process.
   - We should obtain data from Pu production using process to help evaluate potential for use with Pu-238.
   - It has some potential to make spherical granules.
   - Experience exists with Pu and other actinides, especially for vipac and coated-particle applications. However, it is not clear that process would work well with Pu-238 owing to internal heating. If successful, product is one of most dust-free of alternatives. Although not noted in presentation, Russian experience at PO Mayak includes variation of this (Zhemchug) as well.
   - There is a high technical risk and investment for flight qualification.

10. Spherizator Particulate Production
    - As described, this takes oxide, not nitrate as feed. Not applicable to nitrate feed, therefore not consistent with assumptions. Should delete.
    - Does not appear to have an advantage over the Sol-Gel process.
    - There is concern about powder input stream to process. What is the size? Less than 10 μm?
    - Calcium could cause problems.
    - It needs fine PuO2 powder to form the slurry. Not good starting point to eliminate fine particles.
    - High technical risk/cost to qualify.
11. General comments not related to a specific alternative
    - While some categorization was necessary, these processes are not exactly equivalent. It will be important during the subsequent evaluation process to recognize that we should be evaluating the hypothetical "optimized" process or processes that would result from evaluation and optimization of the overall end-to-end process and the individual steps.
    - Reduction of fines should be a process goal for all methods.
    - Minimization of material handling should reduce fines generated through that process.
    - The familiarity and experience varies greatly between these options. The ranking of alternatives can be biased by the team's knowledge of each option. Need to discuss means of removing bias from uncertainty.
    - Too large of particles in the process may add additional problems from self heating, such that individual particles could be hot enough if spilled to damage containment structures.
    - Compared to the current LANL process (manual hands-on and open to glovebox atmosphere), it should be noted that all process alternatives could be viewed as improvements with basic improvements in the areas of automated and enclosed processing, online and at line characterization, and machine enhancements.
    - Every process alternative will need considerable development, but simplifying the process, reducing fines, and improving the process should be well worth the time, effort, and money.
    - As opposed to deciding on a specific method, develop research centers to investigate general processes. For example, a precipitation center or a particle forming center could systematically investigate a number of related processes.
    - We need up-to-date methods of QC to gain information about the PuO2 material at various stages in the process.
    - Improving analytical and computational resources will be essential.

G-6.2 Brainstorming of Must and Want criteria

The committee brainstormed a list of potential criteria for evaluating the alternatives. Members sorted them into criteria the alternative must meet or be eliminated from further consideration. Members also set criteria they want in an alternative.

Must Criteria

1. Meet minimum chemical purity
2. Minimize the fine particles
   - Reduces the production of fine (<10 μm) particles
3. Has to make reactive granules
4. Open porosity (<88% density).

Want Criteria

1. Achieves maximum chemical purity
   - Minimization of impurities introduced from the process.
2. Simple/robust process
   - Ease of automation
   - Recycle of process chemicals
   - Ease of Pu can be recycled
   - Maximize process robustness.
3. Minimize technical risk
   - (State of process development)
   - A proven process versus an immature process that will take work to prove.
   - Has the process been applied to Pu-238?
   - 1. Is it an industrial practice?
   - 2. Has it been demonstrated with U?
   - 3. Has it been demonstrated with MOX?
   - Has it been demonstrated with other actinide?
   - Has it been demonstrated with Pu-238?
4. Minimizes process hazards
   - Minimize hazardous materials in the process
   - Minimize the hazardous waste streams.
5. Granulation size and shape control
   - Granule strength and integrity
   - Ease of densification into a pellet
   - Hot pressable.

G-6.2.1 Screen Alternative through the Must Criteria

The committee attempted to evaluate the alternative against the must criteria and eliminate some of the alternatives from consideration. The committee was not able to eliminate any based on the must criteria, because of the uncertainty of some of the alternatives and the ability to modify or tweak an alternative to address the criterion.

G-6.2.2 Weighting of the Want Criteria

The committee weighted the want criteria. Each participant was given a total of 100 points to allocate among the criterion. There were cautions that owing to the central tendency of statistical allocation of the points, they would have to give a criterion a lot of points (e.g., 50) to have that criterion weighted significantly higher than others when all the participant scores were collected.

The results of the weighting exercise are shown below in Table G-2, where the number in a cell shows the number of participants allocating points with the specified range to a criterion.

The committee reviewed comments the members entered earlier in the day for each of the alternatives. The comments were reviewed for clarification and additional information if possible.

After a brief review of the previous day's results, the final criteria were approved as follows:

1. Achieves maximum chemical purity.
2. Simple/robust process and minimizes in-process inventory within the facility
3. Minimize technical risk and ease of flight qualifications
4. Minimize hazards (radiological, fines, and process)
    a. Minimize radiological risk and eliminate the fine particles
    b. Minimize process hazards.
5. Granulation size and shape control.

The original weights were converted to keep the unweighted and weighted scores in the same scale for ease of comparison. Table G-1 shows the converted weights.

Table G-1. Converted weights for criterion used for selecting alternative for the production of granule Pu-238.

Criterion	Original Weight	Converted Weight[a]
Minimize hazards (radiological, fines, and process)	32.00	1.6
Simple/robust process and minimizes in process inventory within the facility	23.30	1.165
Minimize technical risk and ease of flight qualifications	19.00	0.95
Granulation size and shape control	13.00	0.65
Achieves maximum chemical purity	12.70	.635

a. Converted weight is the original weight divided by 100 and then multiplied by the number of criteria.

Table G-2. Number of participants allocating points within specific ranges for weighting of criterion, Round 2, sorted by total score.

	Points Distribution													
Criterion	0 to 10	11 to 20	21 to 30	31 to 40	41 to 50	51 to 60	61 to 70	71 to 80	81 to 90	91 to 100	Total	Mean	STD	n
Minimize hazards (radiological, fines and process)		2	6		1	1					320	32.00	12.95	10
Simple/robust process and minimizes in process inventory within the facility	1	6		2	1						233	23.30	10.65	10
Minimize technical risk and ease of flight qualifications	3	4	2	1							190	19.00	10.49	10
Granulation size and shape control	6	3	1								130	13.00	8.56	10
Achieves maximum chemical purity	6	3	1								127	12.70	8.07	10

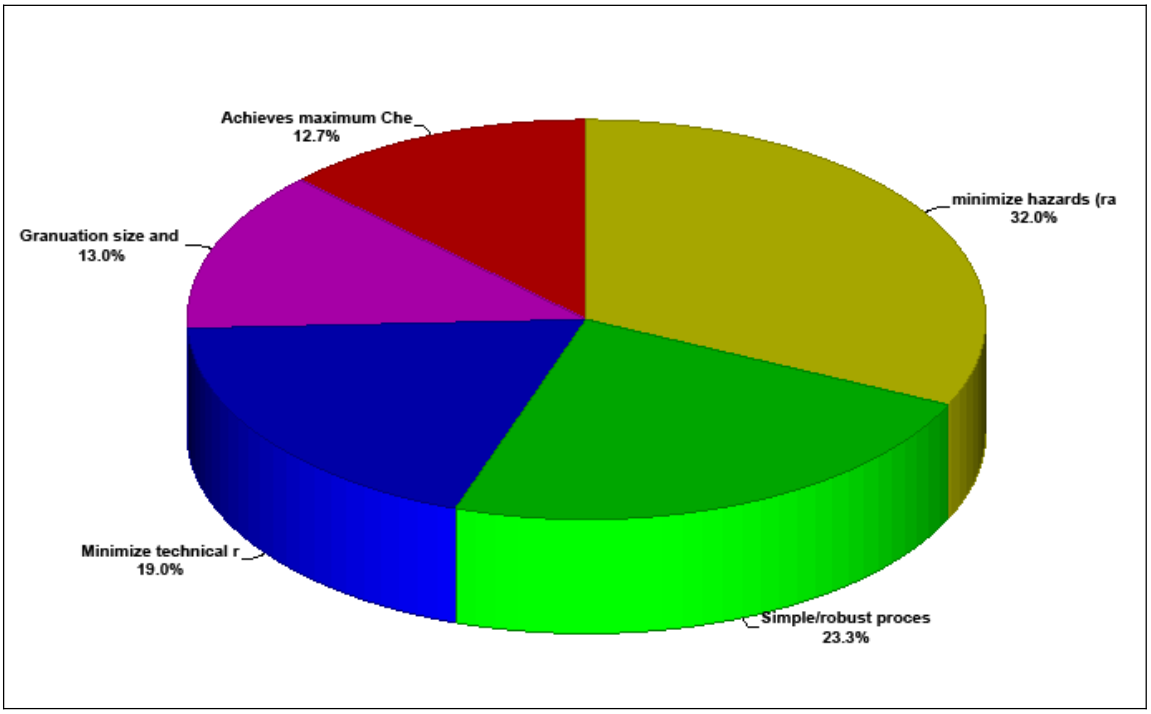


Figure G-1. Unconverted criterion weights to evaluate alternative for granule production.

G-6.3 Scoring Alternatives Against the Criteria

The committee scored the alternatives against the criteria using a 1-10 scale, where 1 meant the alternative scored poorly against the criterion and 10 meant the alternative scored well. Members were instructed to give the alternative they considered the best for a specific criterion a 10, then score remaining alternatives relative to the best, repeating scores if they desired.

It was agreed to score any uncertainty under the risk criterion. If uncertainty existed about an alternative, that alternative should score lower (i.e., more risky) than other, more certain alternatives. Also, the committee was not to consider cost in any of their evaluations or scoring. While cost is important, it will be factored into the alternatives at a later date.

Table G-4 shows the average scores for each of the criteria within an alternative. The color of the cell indicates the level of consensus of the scores within that cell. A green cell indicates a high level of consensus and a red cell indicates a low level of consensus.

A consensus threshold value was set to help focus the group, in the limited time available for discussion, on those cells that had the most disagreement in the scores. It was not intended to imply that the group was in agreement on the score in that cell. The threshold level for consensus was set at 0.60.

Table G-3. Average scores of alternatives against each criterion.

Alternatives	Chemical	Process	Risk	Hazards	Control	Total	Mean	STD	Weighted Total
Weight	0.64	1.16	0.95	1.60	0.65				
1. Current process (baseline)	8.00	3.44	9.90	1.40	4.22	26.97	5.39	3.47	23.50
2. Improved oxalate precipitate	8.56	8.22	8.70	7.20	6.44	39.12	7.82	0.97	38.99
3. Hydroxide precipitate	6.78	6.56	8.10	6.90	6.00	34.33	6.87	0.77	34.58
4. Carbonate precipitate	6.75	5.71	5.00	5.13	5.14	27.73	5.55	0.73	27.24
5. MDD denitration to oxide	6.88	7.67	4.56	6.22	5.38	30.69	6.14	1.22	31.07
6. Russian approach (flocculation)	5.67	6.22	3.60	7.89	6.89	30.27	6.05	1.60	31.36
7. Resin particulate production	4.33	6.00	3.56	7.00	7.11	28.00	5.60	1.60	28.93
8. External Sol-gel particulate production	5.63	5.38	4.00	7.44	7.56	30.00	6.00	1.50	30.46
9. Spherizator particulate production	4.88	3.57	2.30	4.13	7.00	21.87	4.37	1.74	20.60
Total	57.46	52.77	49.71	53.31	55.74				
Mean	6.38	5.86	5.52	5.92	6.19				
STD	1.39	1.61	2.68	2.07	1.09				

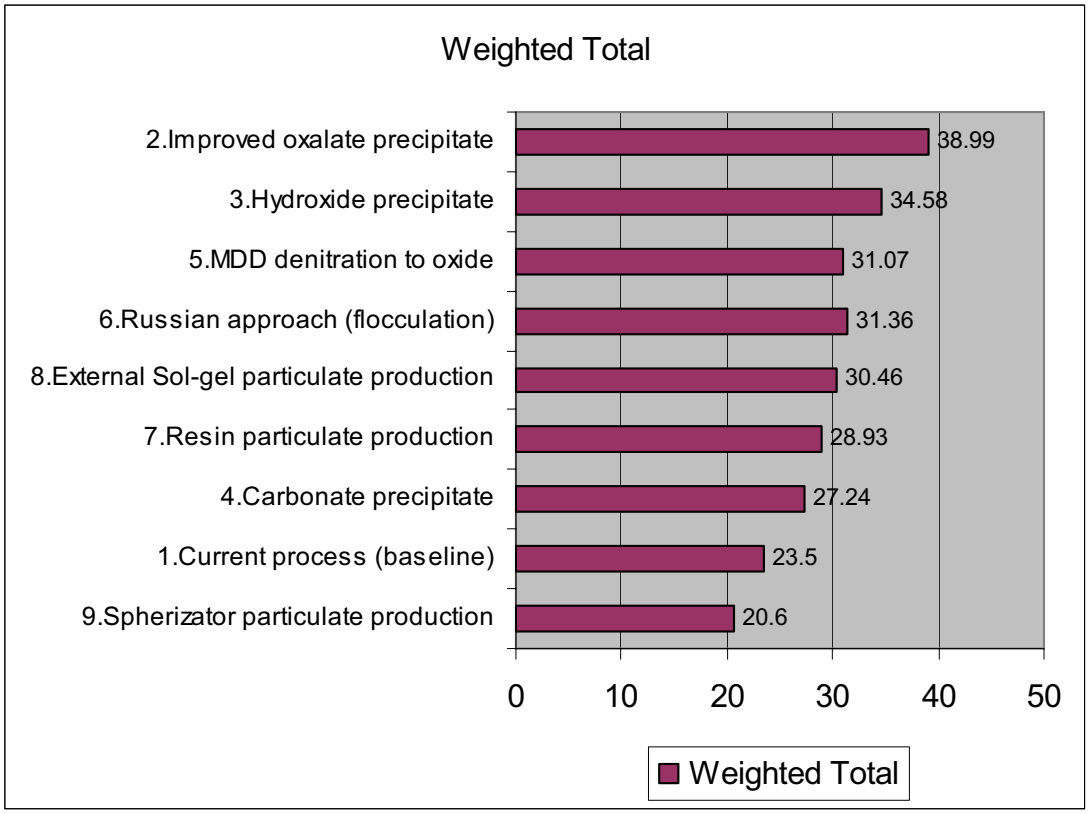


Figure G-2. Weighted total scores for each alternative.

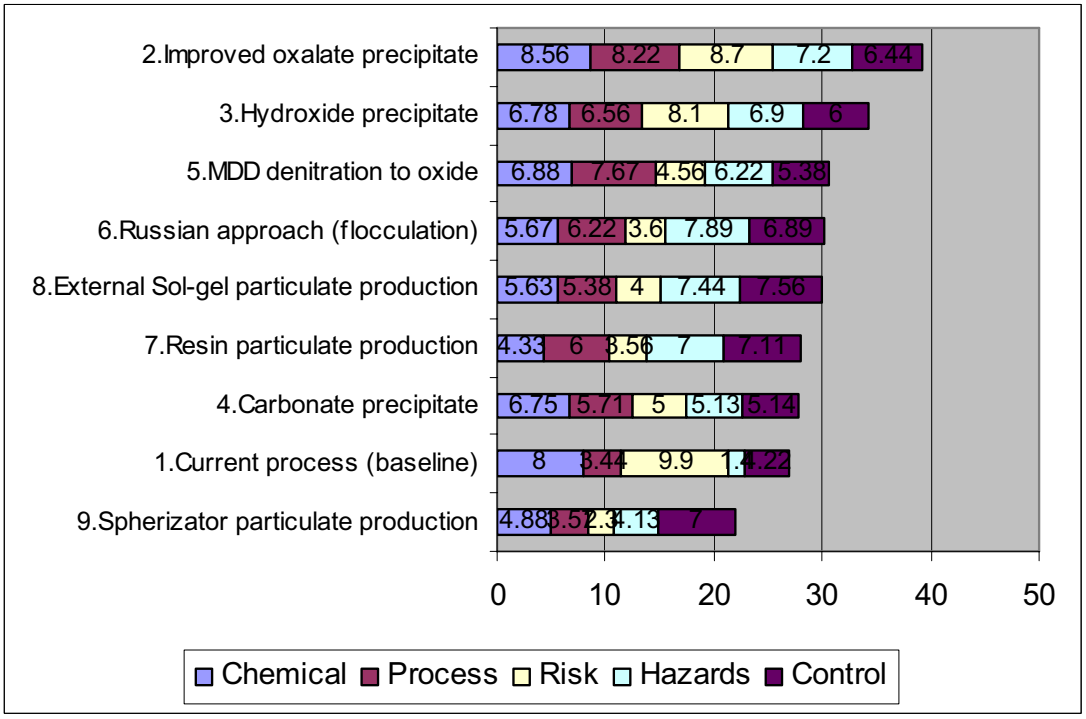


Figure G-3. Unweighted alternative scores by individual criterion contribution.

G-6.4 Alternative Risk Assessment

The committee reviewed the top alternatives for the risks associated with each alternative. Risks were constructed as IF/THEN statements where:

IF something happens, THEN the consequence is …

Each statement was scored as high/medium/low probability that the IF portion of the statement would occur, and a high/medium/low seriousness of the THEN portion. A high score was then converted to a value of 5, a medium to a value of 3 and a low to a value of 1 for averaging all committee members' responses. The committee also added one of the assumptions for a risk analysis.

The committee reviewed the results, but could not totally support the results because of the unknowns in each alternative and the ability to mitigate the risk with additional research into the process.

Table G-4. Average probability and seriousness score for alternative risk statements.

Alternatives	Probability	Seriousness	Total	Mean	STD
1. Improved Oxalate Precipitate					
1.1 IF we make pellets and they don't pass the impact test, THEN how difficult is it to adjust the process?	Lo(1.00)	Me(2.40)	3.40	Lo(1.70)	0.99
2. Hydroxide Precipitate					
2.1 IF we make pellets and they don't pass the impact test, THEN how difficult is it to adjust the process?	Lo(1.60)	Me(3.00)	4.60	Me(2.30)	0.99
3. Russian Approach (Flocculation)					
3.1 F this process cannot handle PU-238, THEN the process is not viable.	Lo(1.60)	Hi(4.80)	6.40	Me(3.20)	2.26
3.2 IF we can't destroy the impurities introduced by the process, THEN we can't meet the chemical purity needs.	Lo(1.20)	Me(3.40)	4.60	Me(2.30)	1.56
4. MDD Denitration to Oxide					
4.1 IF this process can not handle Pu-238, THEN the process is not viable.	Lo(1.40)	Hi(4.60)	6.00	Me(3.00)	2.26
4.2 IF we get impurities from the kiln, THEN we recycle or change the materials of the kiln.	Lo(1.80)	Me(2.20)	4.00	Me(2.00)	0.28
4.3 IF we produce a lot of fines, THEN there is no benefit to using this process.	Lo(1.80)	Me(3.60)	5.40	Me(2.70)	1.27
5. External Sol-Gel Particulate Production					
5.1 IF this process can not handle Pu-238, THEN the process is not viable	Lo(1.80)	Hi(4.60)	6.40	Me(3.20)	1.98
5.2 IF the spheres are not suitable for pellet production, THEN the process needs to be adjusted.	Lo(1.40)	Lo(1.80)	3.20	Lo(1.60)	0.28

Table G-4. (continued).

Alternatives	Probability	Seriousness	Total	Mean	STD
5.3 IF radiolysis or decay heat prevents proper formation of granule or washing of the granule. THEN this option is not viable.	Me(2.20)	Hi(4.20)	6.40	Me(3.20)	1.41
6. Resin Particulate Production					
6.1 IF this process cannot handle Pu-238, THEN the process is nonviable. (Process has been used for high activity materials.)	Lo(1.20)	Hi(5.00)	6.20	Me(3.10)	2.69
6.2 IF the temp gradients are not controlled, THEN the internal heat creates presintering results in a solid structure.	Me(2.40)	Me(3.20)	5.60	Me(2.80)	0.57
6.3 IF you cannot get the right resin and treatment schedule, THEN chemical impurity or pellet fabrication may not be viable.	Me(2.20)	Hi(4.60)	6.80	Me(3.40)	1.70
7. Carbonate Precipitate					
7.1 IF this process cannot handle Pu-238, THEN the process is not viable.	Lo(1.00)	Hi(4.40)	5.40	Me(2.70)	2.40
8.1 IF the assumption is not true, THEN there is additional upstream work needed to reach purity.	Lo(1.67)	Me(2.33)	4.00	Me(2.00)	0.47
Total	24.27	54.13			
Mean	Lo(1.62)	Me(3.61)			
Mode	Lo	Hi			
STD	0.43	1.08			

Current Pellet Production Process by Dennis Bickford

The committee discussed the current pellet process. Dennis Bickford reviewed some of the things that were found to correct problems in the current process.

Sintering

- Sintering increases the structural integrity and density of the granules and provides for better control of densification during hot pressing. 40% of the granules are sintered at 1600 ^{0}C for 6 hr in an argon/O_2 atmosphere to densify the granules to >95% TD. The dense granules reduce shrinkage and cracking during fabrication. The remaining 60% of the shards are sintered at the relatively low temperature of 1100 ^{0}C for 6 hr in argon/O_2 , and act as a bonding agent in the hot pressing.

Blending

- The sintered granules are blended in a ball mill jar at 25 rpm for 15 min. No balls are used. The blend consists of 40 wt % of granules sintered at l600^{0}C and 60 wt % of granules sintered at 1100^{0}C.

Sieving

- To eliminate possible agglomeration during high-temperature sintering or during storage at ^{238}Pu self-heat temperature, the sintered granules are passed through a 210-μm sieve.

Hot Pressing

- Hot pressing is used to control dimensions and shape, rather than to produce a high-density oxide pellet. The blend of sintered granules is consolidated into an integral fuel pellet of the desired shape, dimensions, density, and microstructure by hot pressing at a temperature of 1525 ^{0}C and a pressure of 19.4 MPa. Hot pressing conditions are selected to promote a uniform microstructure with large intergranule pores and to minimize carbothermic reduction of the PuO_2 by the graphite die.

Typical SRS Hot Pressing

In a true double acting press:

- Controlled application of preload to 1.4 MPa using a constant ram velocity of -1.5 mm/s.
- Rapid heating in -8 minutes from ambient temperature to hot pressing temperatures of 1525 ^{0}C.
- Linear increase in load from 1.4 to 19.4 MPa over 5 minutes beginning at 1350^{0}C.
- Five-minute hold at maximum temperature and pressure after die closure.

Vacuum Outgassing

Heating of the fuel pellet at 1150^{0}C for 1 hr in vacuum prior to encapsulation offers two potential advantages:

- Possible reduction in detrimental fuel impurities (e.g., phosphorus and sulfur by evaporation) that decrease the ductility of the iridium, and
- Possible reduction in the O/Pu ratio from 2.00 to -1.99 and a corresponding reduction in oxygen partial pressure that should result in decreased transport of PuO2 Ir, and impurities within the fuel capsule at elevated temperatures.

Heat Treatment

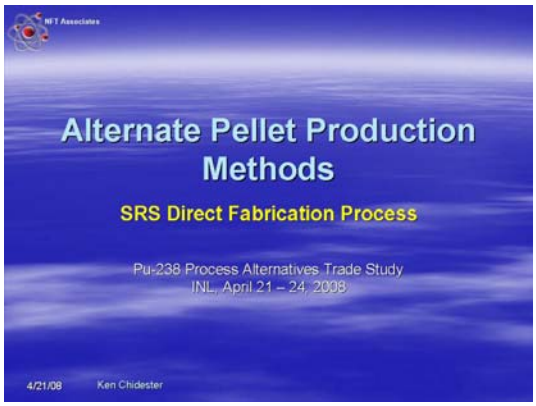
- Heating of the fuel pellet for 6 hr at 1525^{0}C, 250^{0}C above the expected RTG operating temperature, tests for dimensional stability. In addition, the oxidizing atmosphere during heating reoxidizes the fuel pellet from an as-pressed O/Pu ratio of -1.93 to 2.00 and helps to remove volatile impurities such as carbon.

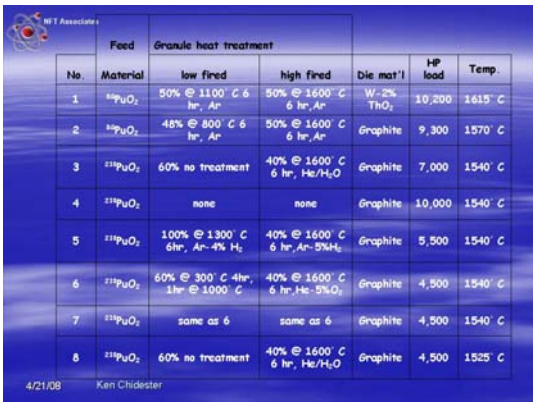
Comments as captured by the facilitators were:

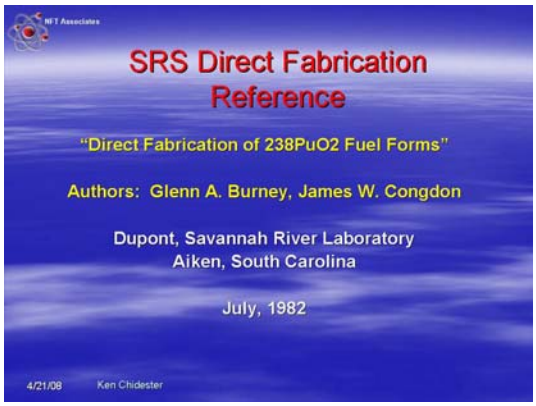
- Pellet gets rounded edge from knife blades.
- The die body is clamped together.
- It requires about l hour to pump down, and pressing process is about l hour.
- It did not vibrate the dies.
- It is loaded to the press with a mechanical arm.
- Temperature comes up slowly -
- The gradients of density are not severe.

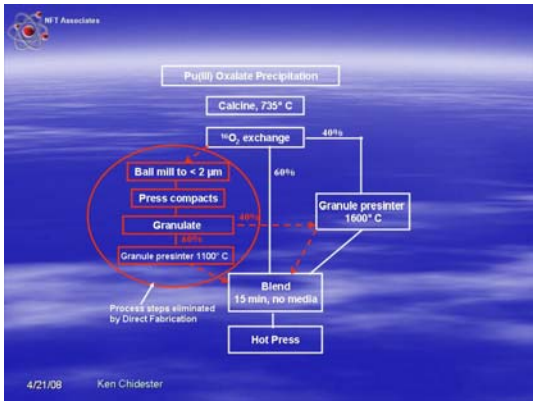
- If the die could be coated, it could be heated longer.
- It uses about a 2000 lb load for 5 minutes.
- It goes through reoxidation heat treatment to demonstrate stability.
- Are there any significant problems with the current hot pressing process? If there is no problem with it now, why do we want to change it?
  - The main problem is the radiation level of the off-gas.

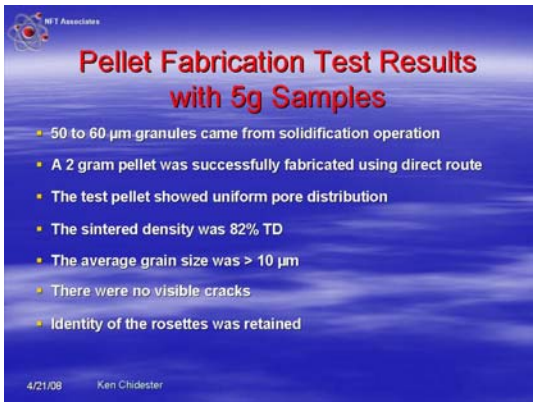
Direct Fabrication by Ken Chidester







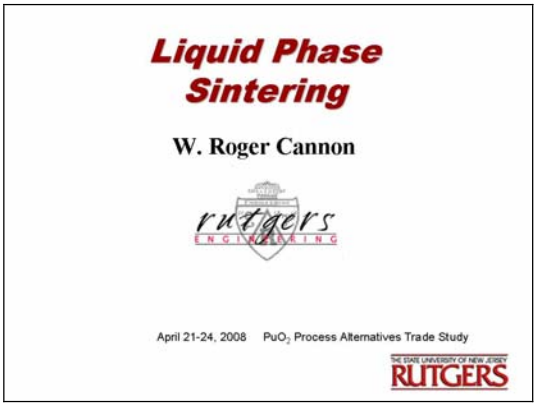


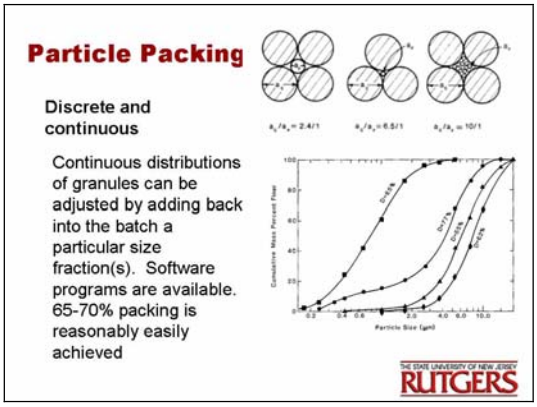


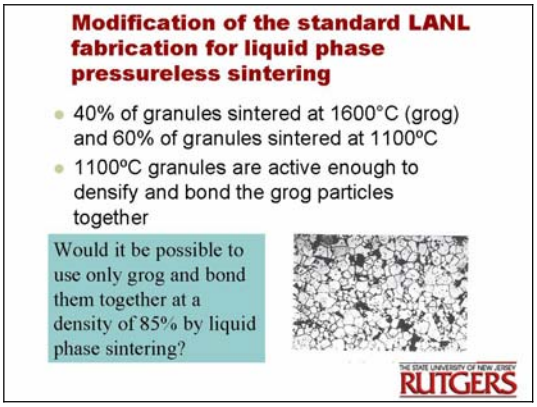
Comments as captured by the facilitators were:

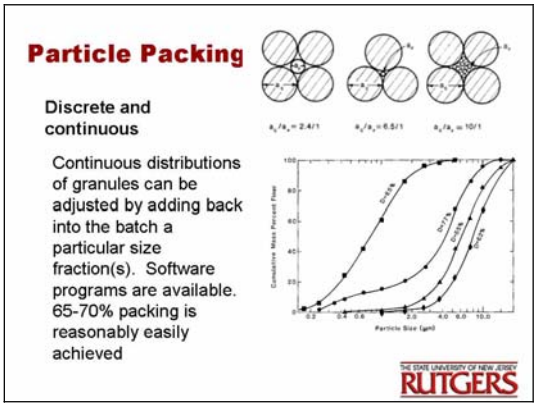
- Line 5 on chart on page 5 should change from 100% to 60%. Line 2 on the same chart should be changed from 50% to 52%.
- Process used in cold or hot press operation.
- Could you get the correct shape?
  - Mound did not think they could do it cold.

Liquid Phase Sintering by Roger Cannon

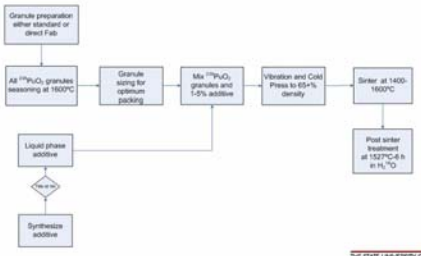






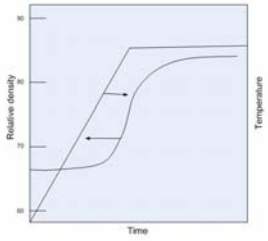


Process flow chart



Stopping sintering at 85% dense

- Transient liquid phase- liquid phase reacts with matrix to form a high melting phase
- Concentration of liquid phase adjusted to stop sintering prior to full densification.



Transient liquid phase example

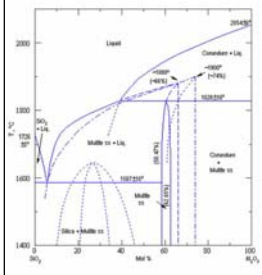
- Elemental Si powder mixed in with 1600ºC sintered granules
  - Two Possible Reactions:

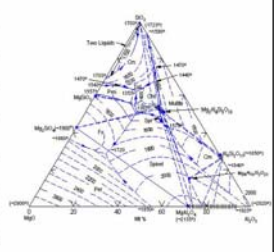
$$PuO_2 + ySi \longrightarrow PuO_{2+x} + Pu_{\frac{x}{2}}Si_y \quad (1)$$

$$PuO_2 + \frac{x}{2}Si \longrightarrow PuO_{2-x} + \frac{x}{2}SiO_2 \quad (2)$$

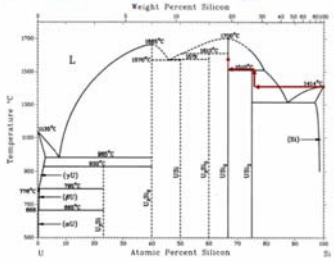
  - Advantage of Si additions is non-radioactivity
  - The following other plutonium silicides are known $PuSi_2$, Pu_3Si_5, PuSi, Pu_5Si_3 and may be added directly

Al_2O_3-SiO_2 and Al_2O_3-SiO-MgO





$Pu_{x/2}Si_y$ (using U-Si phase diagram



Assessment

Positive attributes of process

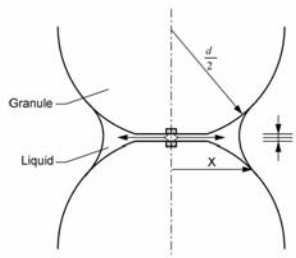
- If successful no radioisotopic fines are introduced
- Shrinkage can potentially be controlled
- Only small amounts of additive are needed for bonding (unknown how much)

Challenges

- **Although some modeling may be done in advance, much experimental work will be necessary to choose the proper system and achieve the proper shrinkage**

Aluminosilicates

- Two GE patents describe liquid phase sintering of UO_2: Al_2O_3-SiO_2 and Al_2O_3-SiO_2-MgO.
  - Surface area of powder 2-12 m^2/g
  - 0.1-1.0% additive
  - 6-47mole% Al_2O_3
- European patent 1482517 describes the addition of 0.02-0.2 mole% alumino-silicate preferably bentonite (25% Al_2O_3) enhances diffusion for better homogenization of MOX



Sintering stress

$$\Sigma = \gamma_{LP}\kappa + \frac{X\gamma_{ss}}{d}$$

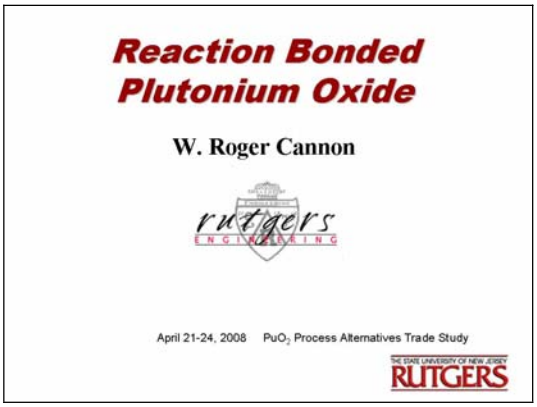
$$X = \frac{z}{2}\rho_s(1-\delta)2\delta$$

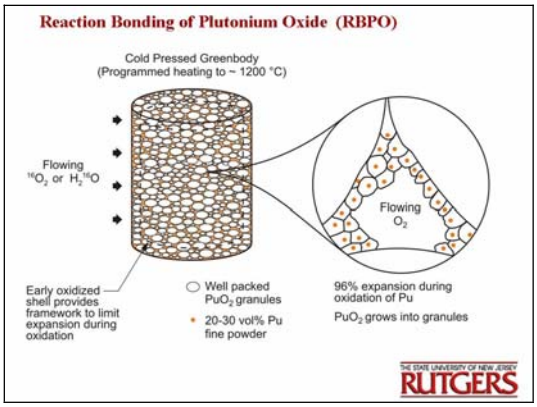
- **Liquid phase must wet the particle**
- **Liquid greatly aids in rearranging particle to pack better**

Comments as captured by the facilitators were:

- Is not hot pressing.
- Process is modification of standard LANL fabrication process for liquid phase pressureless sintering.
- Would it be possible to use only grog and bond with liquid sintering?
- Is it possible in the process to resize?
- The upper limit for granule size is 125 to move forward in the process.
- Is it negotiable?
  - Answer: The procedure is driving the 125.
- The analysis came back as bag of sand.
- Mound hydroxide has too much sand, absorbs cladding.
- 80-85% density possible.
- The shape of the distribution is important.
- Sizing could be improved in any process.
- Because of the impurity issues, this process may not be as viable as originally thought. With the list of unacceptable impurities, it is hard to carry this alternative forward.
- Is there anything that could be used as liquid phase?
  - Limited because of impurities.
- Mostly experimental results with material held at temperature for 1 year or longer.
- This process will have a hard time with any recycling of materials.

Reaction Bonded by Roger Cannon





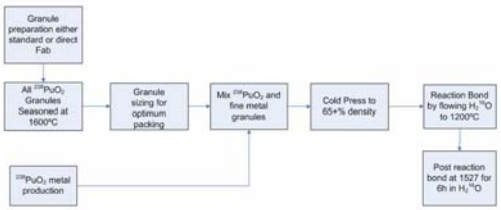
Reaction Bonded Ceramics

Method for fabricating "near net shape ceramics," open porosity, and strong ceramics

- Reaction bonded silicon nitride developed in early 1960's by Jack in England
- Nitrogen bonded silicon carbide widely used refractory
- Directed metal oxidation (DIMOX) developed by Laxide
- Reaction bonded aluminum oxide RBAO developed by Claussen in the early 1990's

RUTGERS

Reaction Bonded Flow Sheet



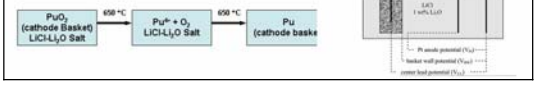
RUTGERS

Plutonium-238 Metal Production

- Plutonium Tetrafluoride Production and Reduction

- Direct Plutonium Oxide Reduction (DOR)

- Plutonium Oxide Electrolytic Reduction



RUTGERS

Predictable density (permeability)

Provided there is neither shrinkage or expansion, the final density is exactly predicted by the (green) density, ρ_i, the fraction of metal oxidized during reaction bonding, f, and the fraction of metal powder, V_M, according to the equation,

$$\rho_{rf} = \frac{\rho_{ri}\rho_M M_{MO} f V_M X_{MO} + \rho_{ri}(1-V_M)\rho_{MO} M_M}{M_M \rho_{MO}}$$

M is molecular or atomic weight, ρ, is theoretical density and X is the inverse of the number of cations in the formula.

Starting density of 65% of theoretical for pressed Pu/PuO_2 pellet with 30% Pu metal powder, the final density would be 84%.

RUTGERS

Advantages of RBPO process

- Near net shape.
- Because the metal powder is ductile it acts like a binder for pressing, giving it a high green strength. In fact, binderless, cold pressed parts can be green machined.
- Reaction bonded ceramics have a high strength. Some RBAO results indicate better strength than sintered Al_2O_3 of comparable porosity.
- High permeability to gases. RBAO has been used as permeable catalyst support because of excellent gas permeability.

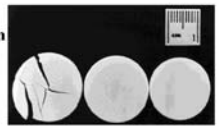
RUTGERS

Challenge

- Prevent runaway
  - oxidation is exothermic
  - $^{238}PuO_2$ is self heating
- Avoid too rapid outer shell oxidation

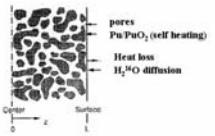
Solution

- Oxygen demand furnace
- Thermogravimetric methods



Air 21%O_2-89%He 10%O_2-90%He

RBAO



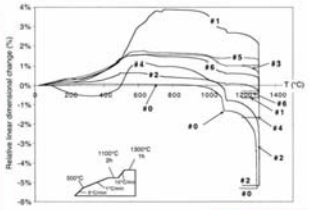
Watson, M. J.; Chan, H. M.; Harmer, M. P.; Carum, H. S. Feedback-controlled Firing of Reaction-bonded Aluminum Oxide. *J.Amer. Ceram. Soc.* **2005**, *88* (12), 3380-3387.

RUTGERS

Near Net Shape

Final dimensions are close to net shape and through processing control can yield either zero and a predictable shrinkage

RBAO example:
RBAO process attrition mills Al/Al_2O_3 to submicron before controlled heat/O_2
Figure to left shows (1) expansion during oxidation (2) sintered shrinkage at high temperature



Bertrand, S.; Michalet, T.; Giraud, A.; Parlier, M.; Bataille, A.; Duclos, R.; Crampon, J. *Ceramics International* **2003**, *29* (7), 735-744.

RUTGERS

Assessment

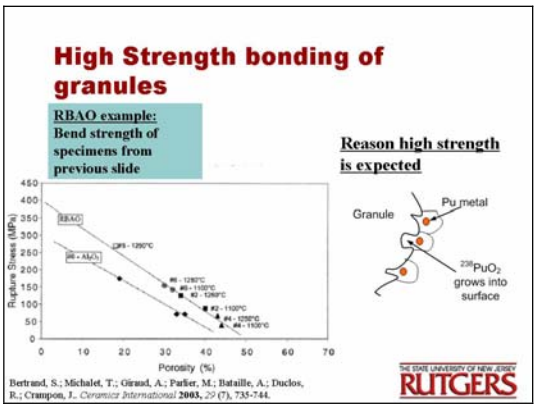
Positive attributes of the process

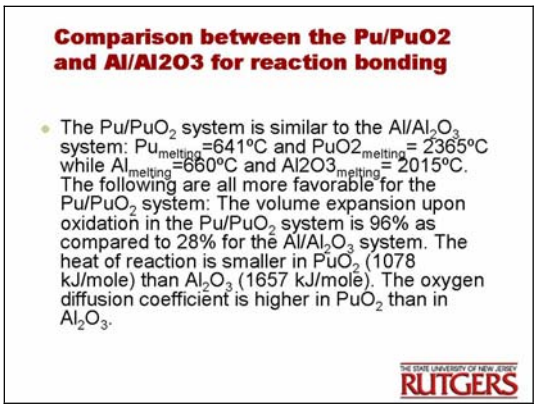
1. Dimensionally and porosity predictable system
2. Eliminates hot pressing
3. High strength but if it breaks, it will break into 1600°C granules sized particles.
4. Developmental work- moderate

Challenges

1. Introduces fine particulate Pu metal granules into process stream

RUTGERS





Comments as captured by the facilitators were:

- RBPO stands for reaction bonded plutonium oxide.
- Pyrophoric metals are difficult for facilities.
- Large volumes of plutonium are volatile.
- If you blend in a ball mill, you cannot open in the air.
- This process produces particles with the same density as the pressed particles.
- Has it been tried with sub-oxides? Use as a sintering aid to reduce the surface.
- Is there experience in materials other than metal?
- Expansion could be confined in a die.
- All granules will be high fired.

Direct Sintering by Paul Lessing

Idaho National Laboratory

Alternate Pellet Production Methods

5.3.5 Preforming Techniques

Dr. Paul A. Lessing

April 23, 2008

FABRICATION OF GRANULE AND PELLET HEAT SOURCES FROM OXALATE-BASED $^{238}PuO_2$

by

D. F. Bickford and D. T. Rankin

Savannah River Laboratory
E. I. du Pont de Nemours and Co.
Aiken, South Carolina 29801

A paper proposed for presentation to the Fall Meeting of the Nuclear Division of the *American Ceramic Society* in Seattle, Washington, October 29-31, 1975

Outline of Presentation

- Goals
- Historical Slugging Method of Preforming Granules
- Limitations of Conventional Die Pressing tall parts
- Dry bag isostatic pressing -- Advantages
- Use of Green-forming Additives (aids)
- Particle Sizing Recommendations for Sintering Methods

TABLE IV

VARIED PARAMETERS FOR INITIAL DEVELOPMENTAL STUDIES

1.	Cold Pressing Pressures:	Two Pressures, 0.4 GPa (58 000 psi) and 0.8 GPa, (116 000 psi)
2.	Feed Granule Size Ranges:	Two size ranges, 0 – 297 μm and 0 – 125 μm
3.	Pre-Press Seasoning Temperatures*:	Four temperatures, 1050°, 1100°, 1200°, and 1250° at a constant time of 10.8 ks (3 h)
4.	Hot Pressing Pressures:	Two Pressures, 20.7 MPa (3000 psi) and 34.5 MPa (5000 psi)
5.	Post-Press Sintering Temperatures*:	Four temperatures, 1000°, 1200°, 1350°, and 1527° at a constant time of 21.6 ks (6 h)

Hot Press at 1530°C and 3000 psi for 20 min

Goals

- Minimize or eliminate use of fine 238PuO2 powder
- Increase Quality Control of final pellets:
  - Final dimensions
  - Homogeneity
  - Porosity (size, shape, total)
  - Reduced cracking during fabrication

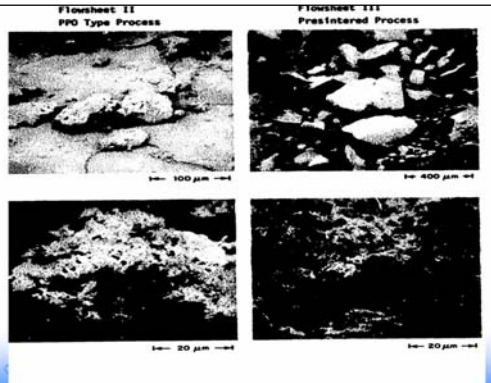


FIGURE 13. Structure of Milliwatt Granules before 1650°C Sintering

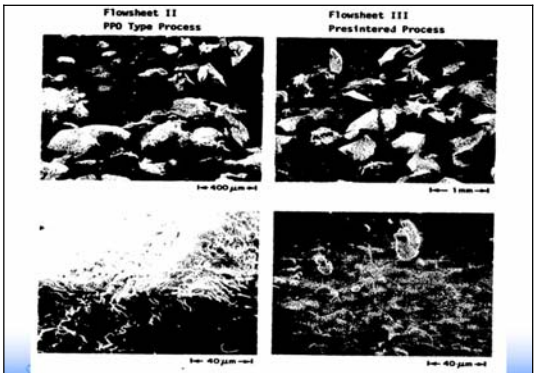
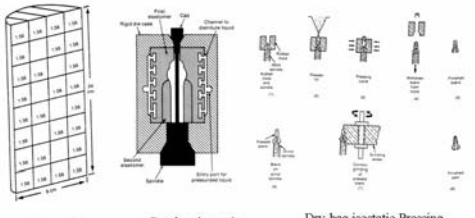


FIGURE 14. Structure of Milliwatt Granules after 1650°C Sintering



Isostatic Pressing Yields homogeneous Pressure and therefore Density

Dry-bag isostatic Pressing could form Pellets or rods in a Glove-box environment

Dry-bag isostatic Pressing Used for automated production of spark-plug insulators and Zirconia oxygen sensors

Previous SRS Conclusions related to Porosity Effects

Both mechanical strength and resistance to sintering are enhanced by rounded, rather than acicular, porosity. Generally speaking, however, the requirements for high strength and for dimensional stability during sintering are in conflict. Strength is enhanced, but stability is decreased, by increasing the ratio of fine porosity to coarse porosity.

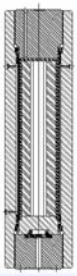
Examples of Dry-bag Isostatic Pressing Machines – Hand operated or Completely Automated versions available. Need feed that flows well.

Ordinary Die Pressing of GPHS shape does not produce homogeneous structure

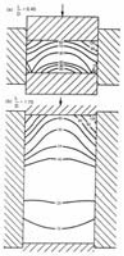
- Large L/D ratio leads to stress/density variations
- Resulting defects:
  - Delaminations
  - End-capping
  - End-rings
  - Hour-glassing
  - Density gradients

Use of Organic binders/lubricants is big problem for 238PuO2 due to heat and radiation: One solution – don't use organics

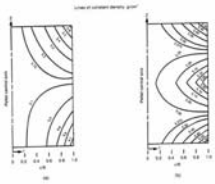
French (CEA) 3-piece die for pressing Am-Containing ceramic without binders



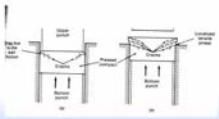
Dry-bag isostatic press tooling + Lubricate walls for release



Pressure Variations due to die-wall friction and particle-particle fricton



Increased uniformity of density by using Double-acting press (right)



Cracks formed during ejection of part from metal die

Use of Binders and Pore Formers:

- AZB (asobenzone or azodicarboxamide) traditional for MOX
- Microcellulose - Japanese pore forming
- New: Char Forming Resins:
  - Furfural (furan-2-carbaldehyde = C5H4O2
  - Phenolic resisn (phenol formaldehyde = "Bakelite")
- New: Inorganic Binders:
  - UO2 hydrated "gells", e.g. Schoepite
  - PuO2 hydrated "gells"

Alternate Pellet Production Methods

5.3.5 Pressureless Sintering

Paul A. Lessing

Idaho National Laboratory

April 23, 2008

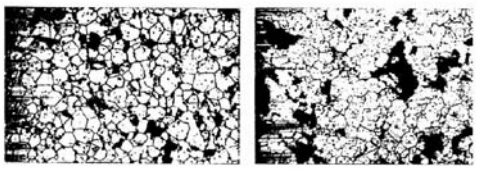
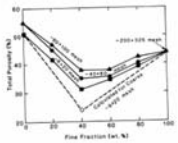


Fig. 5. Comparison of microstructures of 0 – 125μm and 0 – 297μm feed granules. Cold pressing pressure of 0.4 GPa, pre-press sintering temperature (1120°C) and post-press sintering temperature (1527°C) are constant.

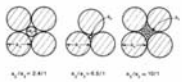
Outline of Presentation

- Historical hot-pressed microstructures from "hard" granules
- Optimized particle packing
- Soft Agglomerates versus Hard Agglomerates
- Spark Plasma Sintering (SPS)
- Superplastic Forming

Maximize Green Density by packing granules sizes



Experimental and calculated porosity For packing of different sizes of Tabular alumina particles



Packing of fine spheres among Coarse spheres – best is ac/af = 6.5

FABRICATION OF GRANULE AND PELLET HEAT SOURCES FROM OXALATE-BASED $^{238}PuO_2$

by

D. F. Bickford and D. T. Rankin

Savannah River Laboratory
E. I. du Pont de Nemours and Co.
Aiken, South Carolina 29801

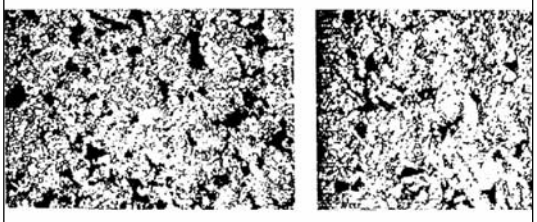
A paper proposed for presentation to the Fall Meeting of the Nuclear Division of the *American Ceramic Society* in Seattle, Washington, October 29-31, 1975

Pressureless Sintering of 238PuO2

Two Approaches:

(1) Use of "soft" agglomerated granules (consisting of fine particles) fabricated using suitable (organic or inorganic) binders/pore formers and dry bag isostatic pressing (rods or pellets)

(2) Use of 100 % "hard" agglomerated granules, graded size fractions to optimize packing, and sintering techniques that "activate" and bond the granules.

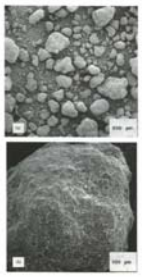


a. 0.4 GPa Cold Press Run P-2 100μm

b. 0.8 GPa Cold Press Run P-10 100μm

Fig. 4. Comparison of microstructures with 0.4 GPa and 0.8 GPa cold pressing pressures. Pre-press seasoning temperature (1150°C) and post press sintering temperature (1527°C) are constant.

Very soft agglomerates (no binders) Easily break up into crystallites during handling.

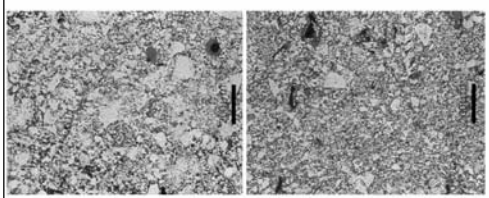


Minimize "Fines" During Handling

"Soft" agglomerates/granules made with binders or pore formers don't shed crystallites as easily and can deform to "mend" together during Green pressing

Surrogate Sintering Study – CeO2 + 5 % HfO2

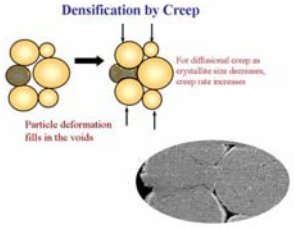
Mixed two types of granules and vary: agglomeration conditions, additives & pressure.
Fixed: High sintering temperature



Sample 3-6 87 % T.D. (100X)

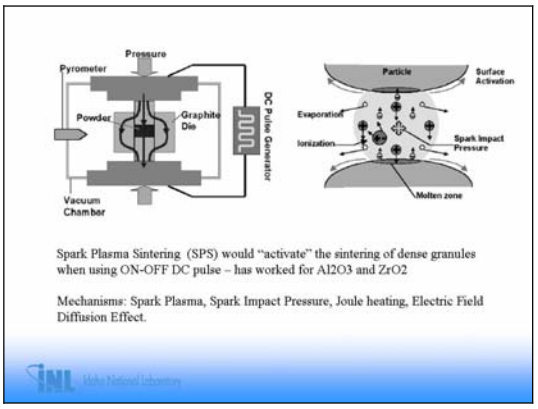
Sample 5-3 82% T.D. (100 X)

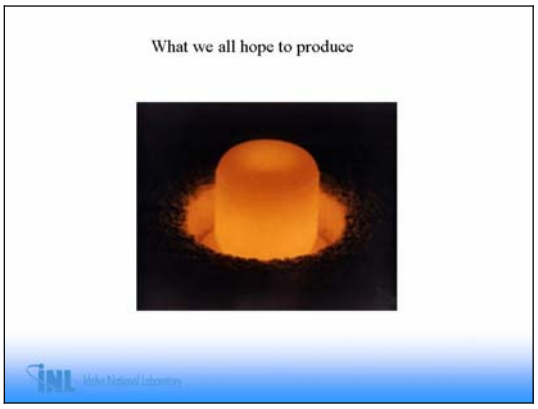
Densification by Creep



Example: Use SPS to sinter hard granules – keep crystallites small (e.g. nano).

Use Hot Pressing to densify via Superplastic deformation & bonding. Then Anneal to achieve grain growth – Prof. Cannon's work.





Comments as captured by the facilitators were:

- Thermal stability of the polyurethane bag (about 200°C) will be an issue with heat source. Could look at cooling loops. There is fluid in the chambers around where parts are pressed.
- If the desired product is an exact shape, a long rod can be pressed and cut into sections and green grind the end. If the binder is correct.
- Pellets or rods can be produced but pellets would take some work. Looking like a sphere is better. Compaction ratio 2.8(?) maximum compaction ratio.
- The fine powder is very sticky. The process needs a feed that flows well.
- Stress variation leads to density variation, which results in defects. Problems with nonhomogeneous matrix causes cracking when pressing of our die. Requires involvement to minimize cracks. Homogeneous and short pellets crack less.
- Better to make a long rod and cut it into pieces. Not for Pu-238 because grinding/cutting for final dimensions produces powder.
- Press to the shape required.
- Could be used in a glovebox.
- Can the process produce pressed slugs out of the die crack free?
  - Yes, normally this can be accomplished.
- Spark plugs have rounded shapes. They grind them green. Recycle the chips and put them back in the unsintered pot. Has been done since the 70's.
- Organic binders have problems. French are pressing without binders.
- Dry bag. Can have bags with rounded corners, no undercuts.
- Pressureless sintering.
  - Fire in air, hydrogen, etc., can switch during the firing process. No graphite dies needed. Preferable to do pressureless sintering.
  - More porosity compared to a normal ceramic.
- Spark plasma sintering (SPS).
  - Does not have to be metal powder, but works for ceramic powders.
  - 500 psi or less.
  - High current, low-voltage pulsing.

  - Activate "clunks" and help sinter together.
  - Densification by creep.
  - Use hard granules, keep crystals small.
- Still faced with the issue of having it qualified for space. Development, testing, and approval process.
- Could eliminate some problems with the cracking, more homogeneous, less cracking.
- Still get desired porosity and density.
- If the spider cracks led to fines, there would be an incentive to do something different.
- Does having fine cracks cause a problem with the impact tests?
- Significant amount of fines inside the iridium.
- Advantage of a more reproducible process, as a batch that is more uniform to characterize the microstructure and test.
- Improving uniformity could allow better understanding of the microstructure to impact testing.
- Theoretical density is around 10 for final product.
- Has compaction ratio of about 2.5.
- Three sizes of granules may provide better density.
- Two sizes may get better packing density (university got 70% with two sizes).
- With bonding would get to 82 or 86% density. Lower compaction ratio provides better product.
- Equalizing the stresses helps.

G-6.5 General Discussion on Specifications at Start of 4/23

The committee reviewed and discussed the pellet alternatives. Because of all the questions, the group took a pause to draw out the flow process for each of the alternatives.

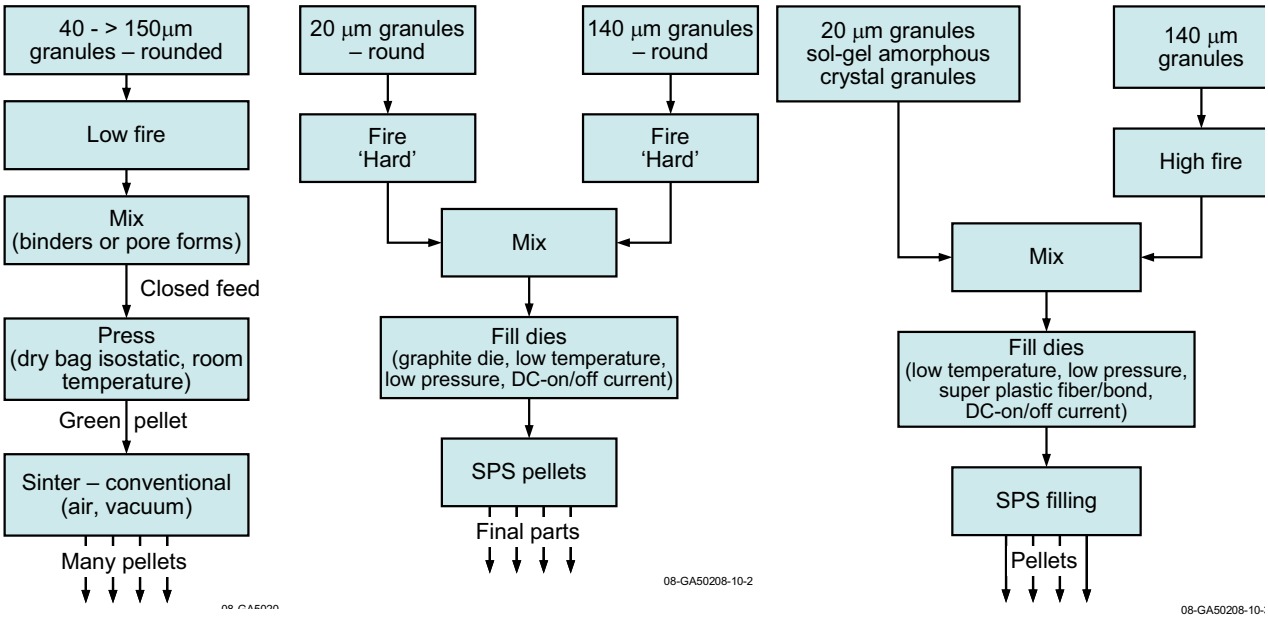


Figure G-4. Flowsheets for isostatic pressing, spark plasma sintering, and superplastic forming.

G-6.6 Participant Comments on Pellet Alternatives Before Scoring

Committee members entered comments on the computers on each of the pellet alternatives, without interpretation or transcribing by the facilitators.

1. Current Hot Press Pellet Production Process
   - Proven process. Limitations have been acceptable previously, but process could be improved.
   - Parameters known.
   - Causes substoichiometry/cracking.
   - Current hot pressing process causes lots of cracking, especially surface cracking.
   - Current process has one-use dies owing to pellet die chemical interactions.
   - Hot pressing is a simple process because the temperature and pressure allow for densification without a lot of surface area in the granules.
   - Equipment design is available and demonstrated for Pu-238.
   - The time limit at temperature combined with surface reduction leads to cracking and potential long-term instability.
   - There are a lot of problems with cracking, especially surface.
2. Improved Hot Pressing (including noninteracting dies)
   - With noninteracting dies, can press also perform heat/atmosphere treatment?
   - Besides die improvements, granule packing improvements would be good.
   - For any new installation, a number of improvements should be considered, including noninteracting punches and dies. If inert containment can be used, increased sintering time/temperature may allow use of less reactive feed granules.
   - Possible coating of graphite dies with vitreous or pyrocarbon, iridium, or platinum group metals to help with release of dies
     - Possible metallic dies, tungsten, molybdenum
     - Dies are probably reusable
     - Reduced pellet cracking
     - Reduced residual stresses in pellet
     - Pellet more stable with respect to sintering forces.
   - Possible graphite die wash with thoria.
   - Noninteracting dies are a good idea. Maybe created by coatings.
   - Possibly heat the die while nearly fixing (or decrease) the temperature of the pellet to release the pellet from the die by differential thermal expansion.
   - More work needed on optimizing of granule size and fractions. Some of this was done at LANL in 1970's. Can we find records?
   - Hot press design available and proven for Pu-238.
   - Some early demonstrations with Pu-238 have been conducted and are promising.
   - Die coating could be applied to several of the alternatives.
   - Product contamination from coating?
   - Noninteracting coatings may cause difficulties for pellet release.
   - As die/punch coatings, chemical vapor deposition of pyrolytic carbon, SiC, ZrC or similar may be considered to produce a reusable set. Issues of bonding and/or chemical interaction should also be considered.

3. Liquid Phase Sintering
    - Preparation of the Pu oxy-chloride will increase the Pu processing. May more than double complexity of processing.
    - Sintering liquid was modified during discussions because of impurity concerns with the originally proposed liquids. This raises the issue of making PuOCl and if it will be an adequate substitute liquid.
    - Can oxy-chloride be generated in situ on granules? If so, may eliminate process steps and potential fine particles.
    - Cl addition to the process may introduce safety issues and materials of construction issues.
    - There is possible risk of contamination from liquid-phase additive, although Cl removal appears to be more straightforward than other known processes.
    - Requires separate process, facility, and inventory for oxy-chloride. Oxy-chloride may not be stable enough.
    - There is a lot of uncertainty with this process. Appears that it will require the most research to identify acceptable materials and develop into a viable solution.
    - While chlorine is not currently listed in the specification, it is not clear how much final impurity of this element would be allowed and to what level we could remove it from the final pellet.
    - This is just at the idea stage.
    - This would allow the use of big, sintered granules (no fines) and still achieve strengthening of the pellets.
    - Recommend a notation in the appendix on chloride salt granulate production (salt dissolution of targets, Np/Pu separation, Pu purification, and PuO2 formation) that this liquid-phase sintering process would probably work well with glassy, dustless PuO2 granules thus produced. The current product routinely achieves greater than 80% bulk density through vibro compaction. That product contains some chlorine holdover (initially) from the precursor salt. If additional chlorine can be added to form the oxychloride on the surface of the PuO2 particles, this might work. If granulate could be vipac-loaded into die and then subjected to liquid-phase sintering for bonding, water-free process would result. Recycle of any scrap would also be quite simple. Removal of chlorine would require treatment of the pellet, but this could be done in the sintering furnace through atmosphere control.
4. Reaction Bonded (sub-oxide Pu powder)
    - Preparation of the sub-oxide powder will greatly increase the complexity of Pu processing.
    - Fine powders may be introduced in preparation of sub-oxide powders.
    - The Pu sub-oxide may contain powders that could be a respirable hazard.
    - Not clear that "fine" metallic powder is required. Use 200 µm oxide and 30 µm passivated metal. Production of Pu-238 metal powder in finely divided form (even 30 µm) will add significant expense and complication from any of the known techniques.
    - Sub-oxide (Pu-2O3) can be easily formed on the surface during calcining by atmosphere control, so no separate handling is required.
    - Requirement of second Pu feed stream complicates.
    - Need to confirm that the conversion from Pu-O1.5 to Pu-O2 would produce desired bonding. May NOT fill interstices properly, but this can be checked in one of plutonium references.
    - Unknown whether the sub-oxide, for instance, Pu-2O3, will expand sufficiently on oxidation.
    - It is good because final density is almost exactly predicted based on initial density and amount of suboxide. Unlike sintering.

- Requires additional upstream processes to prepare metallic (sub oxide) material as input feed
- It is good because initial oxidation of outside layer rigidizes structure, preventing significant changes in dimension. Near net shape.
- It requires substantial R&D effort.
- Use of Pu-2O3 is a better idea than Pu from safety, not technical, point of view.
- Need to confirm that bonding would occur when using Pu-2O3.
- Dimensional control not demonstrated for this product and material.
- Sub-oxide production is not complicated, and can be readily achieved through control of oxygen potential in heat-treatment furnaces at one of the granule formation stages.
- Could add granules to die or closed container and reduce the outer portion to Pu2O3, press, and then pass oxygen through the compact.
- Will look at surface reduction rather than metal.
- Comments about metal are not valid with the assumption of Pu2O3.
- Unlikely to be able to use existing impact test data base.

5. Pressureless Sintering (Dry bag isostatic pressing. Soft agglomeration)

- Produces soft agglomerates.
- Does not have to have a pore former to be successful.
- Process must produce individual pellets of proper shape.
- Reduces pellet handling if process can combine sinter, heat treat and vacuum outgassing
- Significant advantages from added control that is possible, both in green pellet formation and sintering. Optimized end product should be more reproducible (lower variability pellet to pellet) than current or even improved reference process.
- May be difficult to obtain final size and shape.
- This process requires particle sizing to achieve good stacking fractions so that the final densities can be achieved.
- With consistent feed and process parameter development, this approach can make a very consistent and predictable final size shape and density.
- It is assumed in flowsheet that this would be run with all low-fired (active) feed, but it is NOT clear that such a requirement would be necessary. The 40% brick portion could be retained, but probably at the cost of loss of flexibility in the microstructural range. Another way to look at this is that the bricks could be retained at some percentage as another means of microstructural control, combined with pore formers and feed granule optimization.
- It is not clear if this process would be an improvement over improved hot pressing.
- Must confirm that there is no or acceptable surface defects resulting from the mold. The current product appears to retain in some cases ring where rounded chamber meets cylindrical portion of pellet, and that is acceptable without machining, so maybe this is not an issue.
- Pu2O3 added to the surface could aid in increasing the sintering rate initially between large agglomerates, and then be stopped by introducing H_2O to fix the final density.
- Equipment requires adaptation and verification for Pu-238.
- Ability to utilize multipellet furnace for sintering is a clear advantage.
- This process should provide a strong pellet that is stable and crack free.
- Good control of final dimensions is possible.
- There is a big advantage of using furnace with multiple pellets per firing.

- There may be a slight issue with the use of an elastomer bag and the self-heating properties of the Pu-238. Bags may also be single use owing to alpha radiation degradation.
- Low-fired granules may only be 50% dense, so packing granules at 80% means only 40% density total. Can dimensions be controlled? Could half the granules be high fired?
- Use of radiation-resistant pore formers and binders is possible.
- Must confirm that required dimensions including rounded chambers can be achieved with not too exotic bag/mold.
- Have to use low-fired granules, but these should produce minimal fines if handled properly
- Provides much more flexibility to tailor conditions to improve the characteristics of the final pellet.
- Powders can be contained until they are pressed into the green pellet. Therefore eliminates a lot of the problems with production of airborne (fine, respirable) particles.
- Isostatic pressing is superior to pressing in a die to produce pellets with controlled final dimensions.
- Has reduction/oxidation of scrap pellets been attempted as a means to break them apart? For these pellets, thermal shock could also probably be used. If such a nonmechanical dust-free process is possible, this process could be optimized with fixed rate of scrap recycle (standard fuel technique) built into the product. Such an approach would minimize scrap recycle costs, in that most of the scrap should not be chemically contaminated.
- Polyurethane has been shown to be radiation and heat resistant. Powders are in contact with “bag” for only a short period of time.
- Can use release agents on surface of bag, if found necessary.
- The three-piece die is an alternative to dry bag isostatic pressing that may work on one pellet at a time basis. This approach could also be used to press to near final size and lead to controllable shrinkage to final size and density.
- Isostatic pressing yields part that will shrink equally in all directions. Therefore have good control of final, sintered dimensions. Also can eliminate a lot of pressing flaws found from regular dies.
- Probably cannot use existing impact data base.
- Although briefly mentioned in the presentation, considering a significantly different GPHS, such as a stack of pellets or disks, should be noted as a far-out but potentially advantageous option. Short disks are simplest ceramic shape to produce.
- May want to investigate extensive database on "sphere-press" process, which was use of sinterable sol-gel spheres (dustless), as feed to standard cold-press-sinter. Use of isostatic press would be improvement to that of sphere-press process. In that testing, granulate toughness was investigated for retention of residual microstructure from feed materials. It can either be retained or destroyed through press/sinter operations.
- This requires certified pressure vessel. Will impact safety analysis.

6. Spark Plasma Sintering (SPS) (hard agglomerates)

- Although this process appears to be highest risk with greatest uncertainty, if combined with one of the truly dustless processes for granulate production, may yield greatest risk reduction.
- Will not be able to use existing impact test data base.
- This process requires particle sizing to achieve good stacking fractions, so that the final densities can be achieved.
- This requires special size preparation, blending steps.
- It is unknown how much shrinkage will occur. Could be estimated with surrogate study.

- There is good potential to use large granules that are truly dust-free.
- It may be helpful to find a die material that won't interact with PuO_2 but be conductive. The graphite dies may still produce surface cracks.
- Lower temperature and pressures than hot press should lead to more dimensionally stable end product with evenly distributed stresses.
- The process is unproven with use of $^{238}PuO_2$. Will the large granules actually "weld" together?
- Should note in the appendix on chloride salt granulate production (salt dissolution of targets, Np/Pu separation, Pu purification, and PuO_2 formation) that this process is probably most compatible with glassy dustless PuO_2 granules produced by the chloride salt granulate process. The current vipac-oxide fuel product routinely achieves greater than 80% bulk density through vibro compaction. If granulate could be vipac-loaded into die and then subjected to SPS for bonding, elegant and water-free process would result. Recycle of any scrap would also be quite simple because the pyroelectrochemical dissolution process can readily dissolve even high-fired oxide.
- Process would more greatly differentiate types of pores. Larger interstitial pores would form good open porosity network for He release from pellet.
- Determination of connection to existing impact test data base should be based on actual microstructure achieved, and similarity/differences in microstructure compared to existing widely varied experience including hydroxide and oxalate products.

7. Super Plastic Forming

- Could use existing impact data base if oxalate feed used.
- Is not compatible with resin-based feed.
- Oxalate-based feed with low calcine temperature meets reactivity requirement.
- This process requires particle sizing to achieve good stacking fractions, so that the final densities can be achieved.
- If microstructures fall within variability of current and former products (hydroxide and oxalate), should be able to tie to qualification (impact and aging) databases.
- Is actually a variation of the SPS, but requires one portion of granules that has real small crystallites.
- Sol-gel is probably the best approach to produce the 20 μm granules. Could be amorphous when put into the SPS and grow to nano-crystals in-place.
- Can anneal (in place if desired) to grow larger grains at the end of the process.
- Process differentiates pores. Granule interstitial pores would provide nice path for He release.
- Would require some pressure for superplastic forming, so that thicker die is needed than in SPS.
- Superplastic, though allowing high ductility, requires slow strain rates. It might require 1 hour in die.
- Low temperature forming method may be an advantage to forming only a thin suboxide layer.

The group reviewed the comments recorded for the alternatives for understanding and clarity. A fundamental question was raised, to consider whether the product has to be the same as the original product (with just minor changes), or will DOE accept an entirely new product to meet the project needs? The response was that this may be a hard sell politically; however, small-scale testing may be possible to prove the principle. It is better to propose an improved process to get an acceptable product rather than try to propose a new product.

The discussion concluded that the resin process may not be similar enough to the current product (brick and mortar) to qualify as a valid process.

G-6.7 Brainstorming of Want Criteria

The committee brainstormed a list of potential criteria for evaluating the alternatives, starting with the list of criteria for the granule production process. The list of pellet production criteria were:

1. Chemical

   Maintains maximum chemical purity

   (1=Low purity, 10=High purity)

2. Process

   Simple/robust process

   (1=Not simple, 10=Simple)

3. Risk

   Minimize technical risk and ease of flight qualifications

   (1=High risk, 10=Low risk)

4. Hazards

   Minimize hazards (radiological, fines, and process)

   (1=High hazards, 10=Low hazards)

5. Control

   Pellet size and shape control

   (1=Low control, 10=High control)

6. Variability

   Microstructure variability

   (1=High variability, 10=Low variability)

7. Integrity

   Pellet integrity

   (1=Low integrity, 10=High integrity)

G-6.8 Weighting of the Want Criteria

The committee assigned weights to the want criteria. Each participant was given a total of 100 points to allocate among the criteria. They were cautioned that because of the central tendency of statistical allocation of points, they would have to give a criterion a lot of points (e.g., 50) to have that criterion weighted significantly higher than others when all the participant scores were collected.

The results of the weighting exercise are shown below in Table G-6, where the number in a cell shows the number of participants who allocated points within the specified range to a criterion.

The original weights were converted to keep the unweighted and weighted scores in the same scale for ease of comparison. Table G-8 shows the converted weights.

Table G-8. Converted weights for criterion used for selection of alternative for the production of pellets of Pu-238.

Table G-5. Converted weights for criterion used for selection of alternative for the production of pellets of Pu-238.

Criterion	Original Weight	Converted Weight
Process	27.90	1.674
Risk	22.10	1.326
Hazards	15.10	0.906
Control	14.00	0.840
Integrity	10.70	0.642
Variability	10.20	0.612

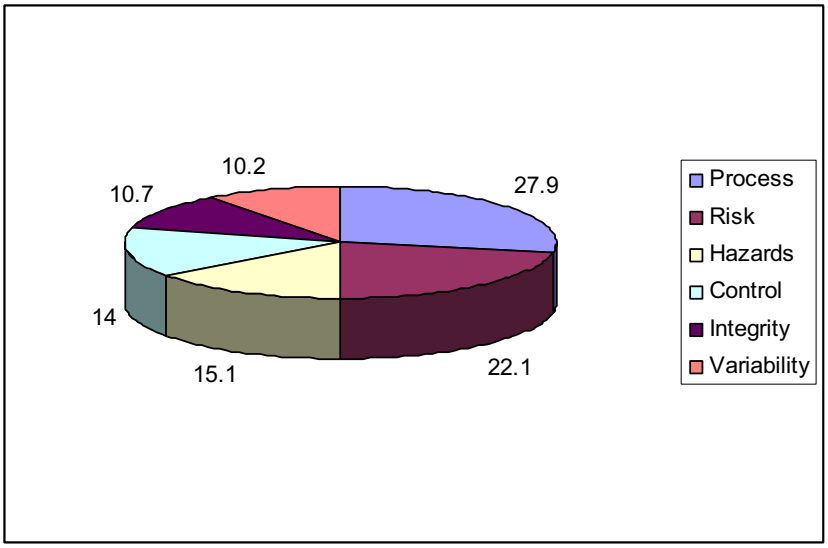


Figure G-5. Unconverted weights for criterion to evaluate alternative to produce pellets of Pu-238.

Table G-6. Number of participants allocating points within specific ranges for weighting of pellet criterion, Round 2, sorted by total score.

	Point Distribution												
Criterion	0 to 10	11 to 20	21 to 30	31 to 40	41 to 50	51 to 60	61 to 70	71 to 80	81 to 90	91 to 100	Total	Mean	STD	n
Process	1	4	3		1		1				279	27.90	18.76	10
Risk	2	2	5	1							221	22.10	9.76	10
Hazards	2	6	2								151	15.10	9.46	10
Control	4	4	2								140	14.00	8.68	10
Integrity	6	4									107	10.70	4.64	10
Variability	7	2	1								102	10.20	8.97	10

G-6.9 Scoring Pellet Alternatives Against the Criteria

The committee then scored the alternatives against the criteria using a 1-10 scale where a 1 meant the alternative scored poorly against the criterion and a 10 meant the alternative scored well. They were instructed to give the alternative they considered to best respond to a specific criterion a 10, then score the remaining alternatives relative to the best alternative, repeating scores if they desired.

It was agreed to score any uncertainty a committee member might have about an alternative under the risk criterion. If there were a lot of uncertainty about an alternative, that alternative should score lower (i.e., more risky) than other, more certain, alternatives.

This table shows the average scores for each of the criteria within an alternative. The color of the cell indicates the level of consensus of scores within that cell. A green cell indicates a high level of consensus and a red cell indicates a low level of consensus.

A consensus threshold value was set to help focus the group, in the limited time available for discussion, on those cells that had the most disagreement in the scores. It was not intended to imply that the group was in agreement on the score in that cell. The threshold level for consensus was set at 0.60.

Table G-7. Average scores of pellet alternatives against each criterion.

Alternatives	Process	Risk	Hazards	Control	Variability	Integrity	Total	Mean	STD	Weighted Total
Weight	1.67	1.33	0.91	0.84	0.64	0.61				
1. Current hot press pellet production process	5.60	9.50	5.22	8.00	4.00	2.75	35.07	5.85	2.51	37.70
2. Improved hot pressing (including noninteracting dies)	8.20	8.80	7.22	9.22	6.11	5.88	45.43	7.57	1.40	47.21
3. Liquid phase sintering (Pu oxy chloride)	4.00	2.20	3.56	5.33	4.88	5.25	25.21	4.20	1.21	23.64
4. Reaction bonded (sub-oxide Pu powder)	5.00	2.90	5.00	6.33	5.67	6.00	30.90	5.15	1.22	29.36
5. Pressureless sintering (Dry bag isostatic pressing–soft agglomeration)	7.30	6.20	7.00	8.00	9.00	9.50	47.00	7.83	1.25	45.08
6. Spark plasma sintering (SPS) (hard agglomerates)	7.30	4.40	8.11	8.44	7.00	7.50	42.76	7.13	1.44	41.57
7. Super plastic forming	5.50	4.20	6.67	8.11	6.67	7.75	38.89	6.48	1.45	36.65
Total	42.90	38.20	42.78	53.44	43.32	44.63				
Mean	6.13	5.46	6.11	7.63	6.19	6.38				
STD	1.50	2.83	1.58	1.33	1.61	2.15				

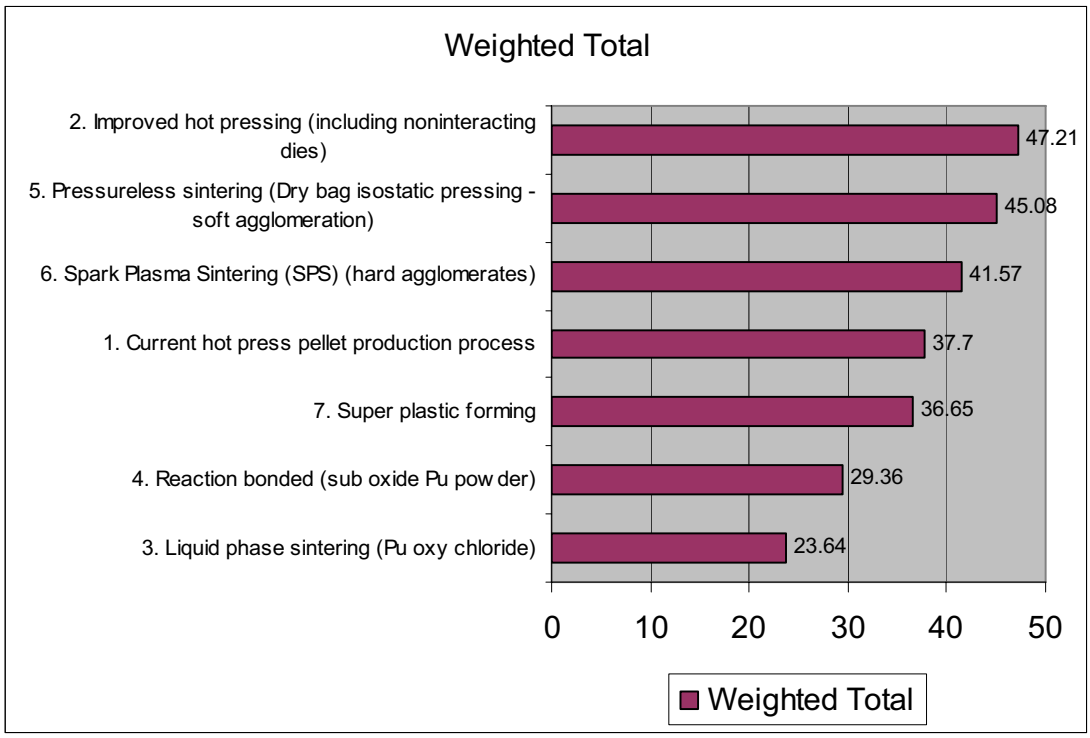


Figure G-6. Weighted total scores for each pellet alternative.

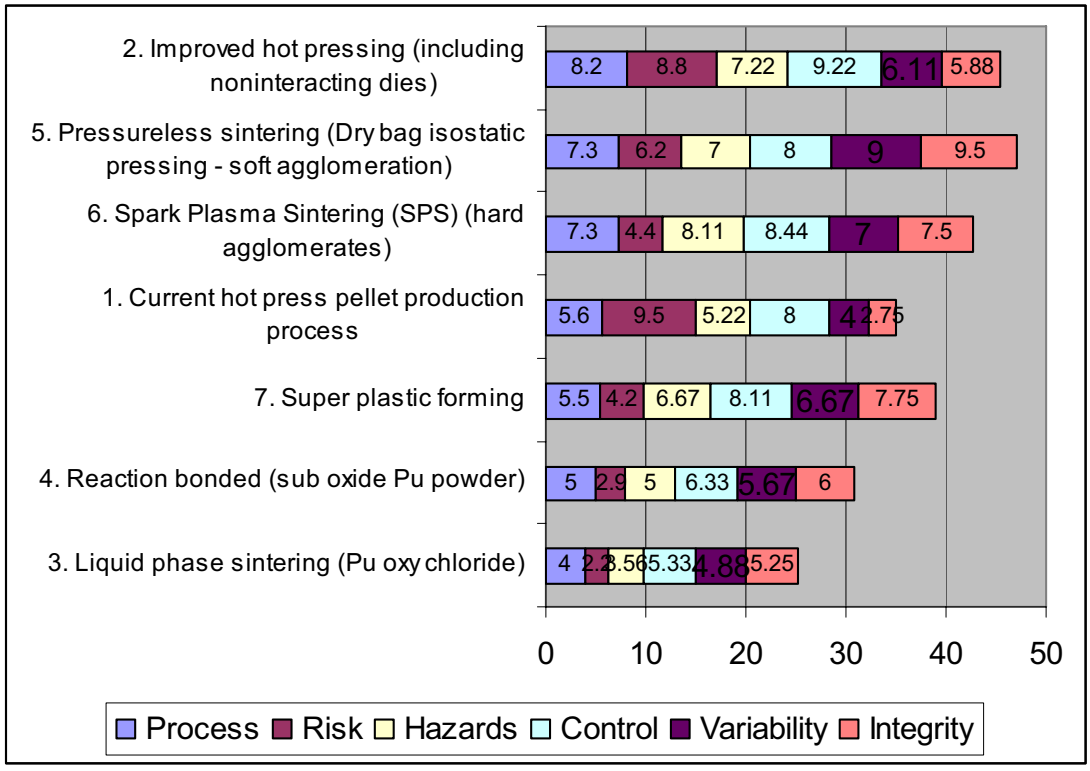


Figure G-7. Unweighted pellet alternative scores by individual criterion contribution.

G-6.10 Alternative Risk Assessment

The facilitator opened the last day with discussion of scoring results from the previous day.

The committee reviewed the top alternatives for risks associated with each. Risks were constructed as IF/THEN statements where:

IF something happens, THEN the consequence is …

Each statement was scored as high/medium/low probability, where high was assigned a value of 5, medium a value of 3, and low a value of 1. The results of this risk scoring are shown in Table G-8.

Table G-8. Average probability and seriousness score for pellet alternative risk statements.

Alternatives	Probability	Seriousness	Total	Mean	STD
1. Improved hot pressing (including noninteracting die)					
1.1 IF the coatings fail, THEN the die still must be changed for each pellet.	Lo(1.80)	Lo(1.80)	3.60	Lo(1.80)	0.00
2. Pressureless sintering (Dry bag isostatic pressing)					
2.1 IF the polymer in the dry bag is wiped out by the heat and radiation, THEN the bag must be replaced.	Lo(1.89)	Lo(1.89)	3.78	Lo(1.89)	0.00
2.2 IF the process will not produce an intact pellet at the correct dimensions, THEN the process will not work.	Lo(1.67)	Hi(4.56)	6.22	Me(3.11)	2.04
2.3 IF the feed variability cannot be controlled, THEN yields go down.	Me(2.33)	Me(3.22)	5.56	Me(2.78)	0.63
2.4 IF we cannot add binders to the process, THEN the green pellets are fragile without sufficient strength to sinter.	Lo(1.89)	Me(2.78)	4.67	Me(2.33)	0.63
3. Spark Plasma Sintering (SPS) (hard agglomerates)					
3.1 IF the granules do not weld together, THEN the process is not viable.	Me(2.11)	Hi(5.00)	7.11	Me(e.56	2.04
3.2 IF the structure does not match the flight qualifications, THEN it fails impact testing.	Me(2.56)	Hi(4.56)	7.11	Me(3.56)	1.41
3.3 IF there is more chemical interaction with the die, THEN the dimensions are off and cracking occurs.	Lo(1.89)	Me(3.00)	4.89	Me(2.44)	0.79
4. Current hot press pellet production process					
4.1 IF the process remains the same, THEN the yields will be low, causing high recycle, and the hazard and radiation exposure is increased.	Hi(4.60)	Me(3.00)	7.60	Me(3.80)	1.13

Table G-8. (continued).

Alternatives	Probability	Seriousness	Total	Mean	STD
5. Super plastic forming					
5.1 IF the grain size is too coarse, THEN the process is slow and dimensions or die interactions are a problem.	Me(2.11)	Me(3.44)	5.56	Me(2.78)	0.94
5.2 IF you cannot maintain the grain fine enough during the process, THEN the process is slow and dimensions or die interactions may be a problem.	Me(2.78)	Me(3.89)	6.67	Me(3.33)	0.79
5.3 IF the surrogate does not behave like Pu-238, THEN you may have a false sense of maturity.	Lo(1.89)	Me(3.67)	5.56	Me(2.78)	1.26
5.4 IF the process is incompatible with Pu, THEN the process will not work.	Lo(1.44)	Hi(5.00)	6.44	Me(3.22)	2.51
6. Reaction bonded (sub-oxide Pu powder)					
6.1 IF the process for reduction cannot be developed, THEN the process is not viable.	Me(3.00)	Hi(5.00)	8.00	Hi(4.00)	1.41
6.2 IF the coating reoxidizes or converts back before firing, THEN the process will not work.	Me(2.80)	Hi(5.00)	7.80	Me(3.90)	1.56
7. Liquid phase sintering (Pu oxy chloride)					
7.1 IF the oxy-chloride does not perform as expected, THEN the process is not viable.	Me(3.40)	Hi(5.00)	8.40	Hi(4.20)	1.13
7.2 IF chlorine is added to the system, THEN impurities may be introduced into the process.	Me(2.20)	Me(2.60)	4.80	Me(2.40)	0.28
7.3 IF the oxy-chloride is not stable, THEN the process will not work.	Me(3.00)	Hi(5.00)	8.00	Hi(4.00)	1.41
Total	43.36	68.40			
Mean	Me(2.41)	Me(3.80)			
Mode	Lo	Hi			
STD	0.77	1.13			

G-6.11 Integration of granulation and pellet alternatives

The committee reviewed the risk results for the pellet alternatives and discussed eliminating the bottom three alternatives from further discussion. It also discussed eliminating some of the granulation alternatives. Key points from the discussion included:

- If the lowest alternatives, based on scoring and risk can be evaluated with surrogates that are less costly, then the tests may provide good results. If they have to be done with Pu-238, then it is not worth proceeding.
- Liquid phase sintering is a simple process, but there is skepticism about whether the process will work. There is a need for assurance that investment in time, money, and energy would pay off.
- Evaluate the four processes that score higher than the current process.
- Super plastic forming scored lower on the weighted basis because of the risk. For the current process, risk is understood, but that isn't true for super plastic forming.
- Granule processes. We do not know the full results of optimization of the processes. In the same hardware, the current process is improved and many variations can use the same hardware. The same equipment can be used for a testing program for improved oxalate, hydroxide precipitate, carbonate precipitate, and Russian approach. MDD equipment is unique, but the equipment exists and Pu-239 could be done in existing equipment. Resin particulate could be done with existing equipment and Pu-239.
- Spherizator. Eliminated because it is ranked below the current process. It requires a very fine particle and unique equipment.
- Current process could run through the precipitation in the new equipment. There is nothing that the improved process can do that is not in the original process. The current process is fine powder, which we are trying to get rid of. We need characterization data from the current process.
- MDD
  - What needs to be proven? What do we need to do? What questions need to be answered to get from surrogate testing to processing Pu-238? How robust is the process for transitioning from Pu-239 to processing Pu-238?
  - Easy process to move from surrogate to Pu-239.
  - What is the definition for the desirable granule structure in a measurable way? What is the acceptable range?
    - Answer: Control of fines, active particle, more spherical, one wide range or two narrow ranges.
  - Lots of uranium experience using this process.
  - Proving with Pu-238 is the final hurdle.
  - Requires large instrument in a hot cell to make the pellet.
  - There is a particle size distribution and morphology that can be used for surrogate trials.
  - Do the surrogate cold. The equipment is not complicated for cold work.
- Resin
  - Technical questions can be answered by surrogates.
  - Desirable from experimental review.
  - What kind of control is there on particle morphology?
  - The process will produce round granules.

  - What is the Sinterability, pressability, flowability of the product?
  - Can be done without Pu-238.
  - Can the reactivity numbers from the surrogates be trusted?
- Sol-Gel
  - If there are limited resources, the process cannot be proved without Pu-238.
  - Investigate the literature on the higher actinide work that has been done.
  - For the purpose of integrating alternatives, the committee eliminated any alternative scoring below, and including, the current alternative (using the unweighted scores). This resulted in a total of 28 potential integration combinations.

G-6.12 Recommendation Discussion

The committee concluded that there was no way to narrow these alternatives further and that the best way to reduce the list was to test alternative methods on a surrogate, then make a decision about which to carry forward for more study.

The committee recognized the commonality of equipment used by the various options, and suggested grouping alternatives into similar test groups.

- Precipitate (including improved oxalate, hydroxide, carbonate and granulation)
- MDD
- Resin
- Hot pressing (including improved hot pressing, SPS, and superplastic)
- Isostatic pressing and pressureless sintering

The general discussion regarding the recommendation and the path forward were:

- Promoting specific technologies can lead to traps. These are the basic processes. Develop options within the structure.
- Look at the modified current process as the preferred option, and next at alternative suggestions where additional benefits justify the increased risk.
- Surrogates
  - Ceria is used for the ceramic properties. It behaves for pressing and sintering in a similar manner.
  - Thoria is too difficult to reduce. It does not answer all the questions and moves the envelope down. The MDD process uses it for starting parameters.
  - Hafnium has been used for mixing and density issues.
- Testing program
  - Define the umbrella of what the project will be doing.
  - Do not commit too far.
  - Goals on the granulation are defined and characteristics are defined in the integration combinations.
  - Too much information may overload and confuse the customer. Look for the big payoffs.
  - Pick things that can easily be done so the benefits can be demonstrated before going to the next step.
  - Getting something useful helps progress the project.

- Deadlines are coming for material availability.
- Be focused on the issues that need solving and that benefit the complex and solve the problem of personnel exposure, increased integrity of the pellet, etc.
- There needs to be clear staging of (1) literature search, (2) cold (surrogate) testing, and finally (3) hot testing of the alternatives.

The committee agreed this was the best path forward. The research needs to be based on findings from the previous research. Let the results determine the path. The research has to be focused and geared to solving issues that have been identified.

G-6.13 Closing Remarks

Comments included:

- There is a good list of sound processes to move forward.
- Trying to apply to the Pu-238 is more difficult.
- Members were pleased with outcome of the exercise.
- The results are agreeable; the specific number ratings are influenced by the nonuniformity of the information on the process.
- Define the feeds, waste products, range of activity, particle size, etc.

Reiterated this needs to be a DOE complex-wide position, not an individual lab recommendation.

- Conclusions should be tightly focused on the committee's vision of future work.
- Evaluate technologies that need more information. This may put us in a better position to evaluate the technologies.
- Members liked the candor of the discussion.
- There is a belief funding will be available in the future, provided it does not come out as a laundry list for research funding.